GENERAL CHEMISTRY

GENERAL CHEMISTRY

AN ELEMENTARY SURVEY

EMPHASIZING INDUSTRIAL APPLICATIONS
OF FUNDAMENTAL PRINCIPLES

BY

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SECOND EDITION, THOROUGHLY REVISED

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PREFACE TO THE SECOND EDITION

In the second edition the opening chapters have been simplified and improvements have been made in the order of presentation. To accomplish this, Part I has been rewritten, having in mind the needs of those who have not had a preliminary course in chemistry. Many additional exercises have been added, to afford more freedom in the selection of problems suited to particular classes of students.

Brief mention has been added of some of the striking recent developments in industrial organic chemistry, such as the direct synthesis of methanol and acetic acid, fermentation methods for the manufacture of glycerol and normal butyl alcohol, and the production of isopropyl alcohol and other non-hydrocarbons from petroleum. On the whole, however, the part devoted to organic chemistry has been somewhat curtailed, in order to gain space for a fuller discussion of the elementary principles of electrochemistry and a better exposition of the subject of precipitation. In this latter connection the researches of Brönsted and others have recently shown how futile are numerical calculations based on the supposed constancy of the solubility-product, in the case of most types of salts. Nevertheless, in a qualitative way, there are still some useful applications that may be made of it.

If the fundamental topics of the first twelve chapters are thoroughly taught, there is a wide range of choice in what may thereafter be presented. The instructor should select such topics as he can make interesting, vivid, and of service in teaching the student to reason chemically, and should be content to omit the rest. Too many try to excavate the entire contents of a text-book by the steam-shovel method.

In preparing the present edition, industrial chemists and teachers of chemistry in many different institutions have furnished useful information, criticism, or general suggestions. The author's thanks are especially due to the following: R. C. Abbott; S. B. Arenson; Harry L. Cole; E. C. Crocker; Norris F. Hall; C. S. Hamilton; Seth Hayes; B. C. Hendricks; Martin Kilpatrick, Jr.; H. H. King; A. H. Low; J. J. Morgan; W. J. Murray; Louise Otis; Francis J. Pond; A. C. Rice; Edward H. Risley; Charles J. Robinson; W. F. Rudd; Herman Schlundt; Fred W. Schwartz; A. M. Schaffer; G. McPhail Smith; H. G. Tanner; W. A. Van Winkle; Otto O. Watts; Harold W. Woodrow.

H. G. D.

SWAMPSCOTT, MASS.,

PREFACE TO THE FIRST EDITION

COLLEGE courses in General Chemistry differ widely in their content and method of development. Some take up element after element and compound after compound, in a purely descriptive way, after the manner of a seed catalogue. Others chiefly emphasize applications of chemistry in the industries. Others, again, with students of some previous training in chemistry, are largely concerned with general principles.

Even when the common ingredients of a course are present in definite proportions, there may be great differences in the manner of their intermingling. In some we have what appears to be a true solution of general principles and industrial applications in descriptive chemistry as a solvent. In such a course the mention of phosphoric acid is seized upon as a pretext for a discussion of the ionization of acids in stages; while copper ferrocyanide occasions a dissertation on osmosis. In other instances the ingredients have a lower degree of dispersion; while at times they constitute a coarse mixture, readily separable by mechanical means.

Such extreme differences in the content of introductory courses or in the method of their development are of course to be deplored, but to some extent they reflect real differences in the needs of the students who pass through them. A special effort has therefore been made to give the present textbook *flexibility*. The purpose has been to encourage the instructor to teach what he wishes to teach, in the order that seems best to suit the past preparation and future needs of his students.

It seemed that this result might best be achieved if general principles were presented in separate chapters, and not too completely scrambled with descriptions of individual chemical substances and applications to industry. Numerous cross-references link up the more theoretical portions of the text with descriptive material that may furnish illustrations of the general principles. The cross-references, furthermore, lessen the danger that wholesale omissions or changes in the order of presentation may render the text unintelligible. Indeed, whenever previous material is very necessary to an understanding of a given topic, the student is given definite instructions to turn back and review.

It is hoped that this book may be appreciated for the things it has left unsaid. Most texts contain too much matter that properly belongs in a course in descriptive inorganic chemistry for students specializing in chemistry. By sacrificing such museum material as hypobromous acid, phosphoryl chloride, hydrazoic acid, and the usual long catalogue of variously colored inorganic salts, space has been gained for the development of such topics of lively interest as hydrogen ion concentration and its applications, an introduction to the chemistry of nutrition, electrochemical principles, and the constitution of matter. This last-named topic, too frequently left as a sort of afterthought, to be presented in a concluding chapter, has been interwoven with the text in such a way that the student examines oxidation and reduction, almost from the beginning, from the modern point of view.

It should, nevertheless, be emphasized that the wide range of topics thus introduced, while providing the means whereby the present text may be adapted to the needs of students of diverse types, makes it more than ever necessary that a selection should be made. The sequence of the descriptive chapters is a common one, but may readily be altered to conform to a laboratory schedule. Material of secondary importance, or of the nature of a digression, has been relegated to small type.

In the exercises at the close of each chapter there is especial need for discrimination. Many of these exercises are too difficult for the average student, and were included for the benefit of those of more than average preparation or capacity. Students receiving a superior grade in the course may be required to demonstrate their ability to solve exercises of this kind. In every class of beginners there are a few who are able to do work superior in quality to that done by others who have had a full year of preliminary preparation. Students of this order of ability are entitled to more consideration than they commonly get. It is easier to hold their interest if the text contains some material difficult enough to try their mettle; while all the members of the class then carry away a better appreciation of what chemistry means, and more respect for its position as a science, than would be possible if they obtained only the mutilated view of the subject that too highly simplified texts present.

For classes without a previous high school course in chemistry, it is best not to introduce the more highly generalized or theoretical topics until some familiarity with the ordinary facts of descriptive chemistry has been acquired. Such students should proceed through Part I at a rather leisurely pace, omitting many of the more difficult portions of the text. The final month of the first semester may then be devoted to a review of the descriptive topics, at which time the theoretical ones, previously omitted, may be taken up.

On the other hand, students with a year of good preliminary training may make rather rapid progress through the descriptive matter, and specialize on the very topics that beginners must postpone or omit. Those who have not had a course in high school chemistry commonly recite more frequently than those who have; hence the two classes of students should be about equally advanced from about the middle of the second semester. The year may then be closed with a review of the important general principles (tabulated at the close of the Table of Contents) or devoted to a study of the special topics most likely to be useful in the students' future work. Much of the descriptive chemistry of the metals may commonly be omitted, except in so far as it may be used to enliven discussions of general principles.

Indeed, though the course may well begin by being largely descriptive, general principles should receive chief emphasis in the end. Even with students who are to specialize in chemistry, the purpose of a first course is not so much to impart information as to disclose a point of view. The facts of chemistry are but the raw materials from which must be synthesized a certain state and quality of mind.

H. G. D.

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A study of the properties and transformations of matter and energy.

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GENERAL CHEMISTRY

Part I

PRELIMINARY

CHAPTER I

INTRODUCTION

1. What Chemistry is About.—The science of chemistry has three chief problems: (1) **To take note of the qualities by which different kinds of matter are distinguished from one another.**

What qualities has iron, that enable it to be recognized as iron, whether the actual **object** concerned is a ten-penny nail, a sledge-hammer, or a meteorite? What qualities do a diamond, a pencil "lead," a lump of coke, and the smoke of a locomotive have in common, that permit us to recognize them all as consisting, in the main, of the one kind of matter called carbon?

(2) **To find means for separating different kinds of matter, when they are intermingled or combined with one another.**

The chemist is able to separate air into nitrogen and oxygen, with smaller amounts of about half a dozen less common gases; or a five-cent piece into copper and nickel, with perhaps traces of gold and silver; or petroleum into gasoline, lubricating oil paraffin, and a number of other things.

Very often such a separation of one kind of matter into its several constituents is merely for the purpose of *identifying* the latter. So well has this part of the problem been solved that you may send a properly qualified chemist almost anything, from a patent medicine to a rare mineral, and get from him a pretty good idea of what it contains.

(3) **To discover the means and conditions for changing any given kind of matter into other kinds.**

The chemist mixes sand, lime, and soda, and converts the mixture into glass; or treats cotton with a mixture of acids, to convert it into cinematograph film; or heats coal in an oven, to produce coal-gas, ammonia, tar, and coke.

The new kinds of matter obtained in such transformations are often of a most unexpected sort. Who but a chemist would ever guess that common salt can be resolved into a greenish gas and a silvery white metal? Or that a diamond, if heated, is converted into graphite? Or that two odorless gases, nitrogen and hydrogen, can be combined to form ammonia? Or that ordinary air and water can be made to produce such a corrosive liquid as nitric acid?

So astonishing are these changes, and so readily do the different types of matter appear to assume new qualities, that one might be tempted to assume the possibility of transforming any kind of matter into any other. Can carbon be transformed into copper, or lead into gold? The answer is, *not at present;* perhaps, or probably, *never.* That question will be discussed later (§ 13). But chemistry has not yet solved its three chief problems; so, after all, *who knows?*

2. The Subdivisions of Chemistry.—Chemistry, then is **the science concerned with identifying, separating, and transforming the different individual types of matter.** Its progress, during a century and a half of development, has been so very rapid that no one person can now hope to master the whole of it. Instead, each chemist specializes in a certain portion of the field, coöperating with workers in some one of the other sciences that border on chemistry and make use of its results.

The chemical problem of *identifying* is now so well advanced that more than 300,000 different types of matter have been recognized and listed, with their chief characteristics, in the great catalogues of **Descriptive Chemistry.** The search for means of *separating* has resulted in the numerous procedures of **Analytical Chemistry,** which enable the chemist to proceed systematically in finding out what things are made of. Its study of means and conditions for *transforming* one kind of matter into another has resulted in the discovery of tens of thousands of new types of matter. This is **Synthetic Chemistry,** classified as **Organic,** if it deals with products containing carbon; and otherwise as **Inorganic.**

Finally, we have **Theoretical,** or **Physical Chemistry.** This takes note of the general principles or scientific laws determining the conditions that must be observed in effecting transformations of matter. Since physical chemistry tries to get at the reasons why things happen as they do, every discovery in this field, however far removed from everyday affairs, is apt to have some unexpected practical results.

The course that the student is here beginning can give only a hasty glimpse of the broad outlines of the subject— a knowledge of chemistry comparable to the knowledge of a university that one might acquire from an afternoon's tour of the campus. This is admitted by the very title of the present text-book—*General Chemistry.* Still, a student in such a course ought to catch something of the spirit of the science, realize the important part that it has played in molding civilization during its century and a half of existence, and have some vision of the directions in which it is likely to develop in the future.

3. Chemistry as a Part of a General Education.—The applications of chemistry in agriculture, biology, dentistry, medicine, and the various branches of engineering are a sufficient excuse for its inclusion in the training of students preparing for careers in these special fields. But its importance as a part of a general education has been insufficiently emphasized.

The so-called cultural studies are those that summarize the principal intellectual achievements of the human race, and permit us to review the most noteworthy things that the mind of man has produced in centuries gone by: masterpieces of literature and art, systems of law and government, ideas of logic and philosophy, triumphs of architecture and engineering, and the great generalizations of science. Among all these, science holds first place in the seeming sureness with which it makes progress, and the promise of permanence in its results. Daily, and more and more, it influences the lives (and thoughts) of all of us—poets and portrait painters, no less than physicians and engineers.

Chemistry, in particular, serves as a splendid illustration of what science is, and why some knowledge of its methods and results must be obtained by everyone who hopes to become well educated. Modern chemistry, with its far-reaching generalizations and hypotheses, is a fine example of how far the human mind can go in exploring the unknown beyond the limits of human senses. Its industrial achievements, though the wonder of the age, are the least of the reasons why anyone should study it; and many who are first attracted by its reputation for practical utility, in the end have come to prize it most for its intellectual beauty.

Chemistry has points of contact, too, with subjects at first sight quite unrelated. The pages of biography and history bristle with chemical references for those who can read between the lines; while for one who seeks recreation in travel, a little knowledge of chemistry will do much to beguile the way. Deposits of sulfur in the grottoes of Vesuvius, enameled beads in a museum, trays of black tea on a hillside in Japan, salt basins along the coast of China, betel-nuts in the Philippines—these all speak of chemical processes, and have a heightened interest for one who has studied chemistry.

It is no less true that a little scientific knowledge may influence one's opinions on subjects quite remote from scientific things. The student of chemistry comes to know something about the geographical distribution of the resources of the globe, and finds it easier to understand the economic motives behind the great wars of history, and to perceive what influences have been at work in the making of treaties. He also learns that the earth's stores of coal, petroleum, metallic ores, and minerals were formed by very deliberate processes, requiring thousands of years for their accomplishment. Should these material blessings, provided by Nature for all the generations of men, be dissipated without regard to the needs of those who are to come after us? Chemistry, here, can teach a moral lesson.

Thus, for those of us who make only a brief study of chemistry, the benefits to be expected are of an indirect nature. *Increased capacity for enjoyment, a livelier interest in the world in which we live, a more intelligent attitude toward the great questions of the day*—these are the by-products of a well-balanced education, including chemistry in its proper relation to other things.

Refer also to Conclusion.

4. Materials and Their Properties.—The different kinds of matter occurring in nature or prepared artificially are called **materials.** Iron is one material, water another, glass—or, more properly, each special kind of glass—another. The qualities that serve to distinguish a given material from others are called its **properties.** Iron has the property of rusting in moist air; water the property of dissolving sugar; sugar the property of being dissolved by water; glass, the properties of brittleness and transparency. But note that size and shape are not properties of materials, but rather *attributes of particular objects.*

The chemist is interested in the properties of materials, not only as a means for distinguishing them from each other, but because **properties determine uses.** Rubber might still have its uses, if inelastic; or sugar, if tasteless; or coal, if incombustible— but they would not be the uses of to-day. The study of chemistry, then, is to a very large extent a study of properties.

Now the different kinds of matter in the world about us are quite numberless, and each of them has its own special set of properties. Chemistry would thus be bewildering and hopeless were we not able to simplify it by selecting for special study a few kinds of matter that serve as types for the rest. We shall find that potassium, within limits, behaves like sodium; that all acids have certain properties in common: and that when we have studied one alcohol we know what general behavior to expect of all the rest.

Physical properties are those that may be expressed without considering the possibility of transforming the given material into materials of other kinds. Among these are included familiar properties directly perceptible to our senses: color, odor, taste, relative heaviness. The capacity of a material for being dissolved in water or in some other solvent is also commonly listed as a physical property, for most chemists would not consider a solution formed by dissolving sugar in water as being a new material, distinct from both sugar and water.

The **chemical properties** of a material are those that express its capacity for being transformed into other materials. Thus, iron has the chemical property of being transformed into iron rust, by contact with moist air; the organic matter of a cigar that of being transformed by union with the oxygen of the air into invisible gases, smoke, and ashes; the sugar of apple juice that of being transformed into alcohol and carbon dioxide gas, by fermentation.

The physical properties of a material are often the most *convenient* means of identifying it; but its chemical properties are the most *conclusive*. Thus, a diamond, a pencil "lead," and a lump of coke differ much in color, hardness, relative heaviness, and other physical properties. But they all agree in the chemical property of being able to unite with the oxygen of the air to form an invisible gas, carbon dioxide; and they are accordingly recognized as different forms of one material, carbon. Similarly, ice, water vapor, and liquid water are different forms of water.

5. Physical and Chemical Changes.—We have noted that one of the three chief problems of chemistry (§ 1) is to discover the means and conditions for changing any given kind of matter into matter of other kinds—any given material, that is, into new materials. But let us note a distinction. If we heat a piece of iron red hot, is it then to be regarded as a new material, distinct from that with which we started? Not only its color but several other important properties have been altered; for red hot iron is no longer attracted by a magnet, and its relative heaviness (specific gravity) is distinctly less than that of cold iron. Still, these are all physical properties. In such chemical properties as express its behavior in the presence of other materials, it remains unaltered. It will still rust, in contact with moist air, and will still be corroded by acid vapors—and more readily, indeed, than at lower temperatures.

Thus iron that has been heated red hot is still iron. It has merely had some of its physical properties altered— has experienced **a physical change.** Other physical changes are those produced by melting ice, turning water into steam, magnetizing iron, softening copper by heating it to redness and plunging it into water. Many of the physical properties of the original material are altered in each case; but its chemical properties remain unchanged, and these permit it to be recognized as the same material that we had in the beginning.

In a **chemical change,** on the other hand, *all* the properties of a given material are so completely altered that we give the material a new name. We say that we have **chemically transformed** it into one or more new materials. Physical change, dry some wood. Chemical change, burn it up. Other examples of chemical changes are the rusting of iron, the digestion of food, the fermentation of apple juice.

The alteration of physical properties in a physical change is often *slight*, *gradual*, and *temporary*. Magnetized iron is not appreciably different, apart from its magnetism, from ordinary iron. Red-hot iron acquires its redness gradually, as the temperature is raised, and loses it again when the source of heat is withdrawn. Compare this with the *profound*, *sudden*, and *permanent* alteration of the properties of a stick of dynamite, when it is exploded. Still, physical changes at times do produce a profound and sudden alteration of physical properties, as when ice melts; or a change that is permanent, too, as when a diamond, by heating, is converted into graphite. The essential difference, after all, is that in physical changes *only a few* properties are altered, and only physical properties. In chemical changes, *all* the old properties disappear, and completely new properties appear. Did they not, ashes and cinders might be worth as much as coal.

6. Molecules.—But why should the alteration of properties involved in a chemical change be so amazingly thorough and complete? A possible explanation is suggested if we consider a carload of wheat. Subdivide this into smaller and smaller lots, and each of these will still retain all the properties characteristic of the original material. But the ultimate units are the individual grains of wheat. To subdivide these would be to deprive the wheat of its most remarkable property—its capacity for germination. We should then have something different—bran, middlings, and white flour.

So with matter in general. Its properties in bulk are retained for a time as the scale of things is reduced. A single droplet of mist is identical with a bucketful of water, in so far as concerns the *kind* of things that it will dissolve. Under the microscope we can often observe chemical changes proceeding with the formation of crystals invisible to the naked eye, yet easily recognizable as being of the same kind that we should obtain in dealing with visible amounts of material. And the perfume that pervades a room from a single tuberose is none the less distinctive, though it represents an invisible and utterly unweighable amount of matter.

Still, the analogy of the carload of wheat suggests that matter in general may not continue to retain its properties when subdivided without limit; that each kind of matter may be composed of definite ultimate particles; and that physical changes leave these particles intact, while chemical changes decompose them. Other facts—indeed, all those embodied in the physics and chemistry of to-day—support the same conclusion. Thus we presume that were we possessed of microscopes vastly more powerful than any now made we should perceive all matter, even the densest metal and most solid stone, to be *discontinuous;* to be made up of separate ultimate particles, whose character determines the properties of the matter as a whole. We call these **molecules.**

What molecules would look like, were we actually able to see them, we cannot imagine. They certainly would not "maintain all the properties characteristic of larger samples of matter of the same kind." For as we divide and subdivide a material until the fragments become of microscopic size, we may progressively alter its color, and some other physical properties as well. But at any rate, **the properties of each kind of matter are determined by the character of its molecules;** and were the molecules in any given sample of matter to be resolved into smaller fragments, the matter as a whole would thereby be transformed into matter of a different kind.

This view of what we should find, were we able to examine portions of matter indefinitely made smaller and smaller, is called **the Molecular Theory.** *Hazarded at first as a mere guess,* many centuries ago, it has played so important a part in the development of modern science that it would be very difficult—and besides, very useless—to postpone applying it in our study of chemistry. Furthermore, the evidence of the past few years has convinced the chemist of to-day of the actual physical existence of molecules. To him, the individual molecules of the air he breathes are as real as the individual books that compose his library. Thus what began as a guess became later a well-supported theory, and ended by being regarded as established truth. A chemist, in considering a chemical change, generally thinks in terms of molecules, though his thinking is guided by the properties of matter in bulk. And since our purpose is to learn to reason about things chemical as a trained chemist might do, let us accept his molecules from the beginning, though the most impressive reasons for believing in their existence will become apparent only at a later stage in our progress (§ 32).

7. Mixing, Dissolving, Reacting and Combining.—To **mix** several materials is to intermingle them. One of three things may happen:

1. The intermingled materials may have practically no effect on each other. The resulting mixture will then have properties *intermediate* between those of the materials from which it was prepared. We see this happen when an artist blends pigments.

2. The materials may act upon each other in such a way as to *reduce the size* of the intermingled particles. Thus, crystals of sugar, mixed with water, are reduced in size by the loss of material that is stripped away from their surface and dispersed through the water. If we have reason to believe that the dispersed material has been reduced to its very molecules, we say that it is **soluble** and that we have **dissolved** it. The resulting mixture of different kinds of molecules, as distinguished from one of different kinds of coarse particles, is called a **solution.** (Read § 91.)

3. The materials may act upon each other in such a way as to be *chemically transformed.* We then say that they have **reacted,** or have entered into a **chemical reaction.** When sugar is mixed with water it merely dissolves. But baking powder, in the presence of water, reacts, liberating bubbles of carbon dioxide gas. The water enables the molecules of the two principal ingredients of the baking powder to act upon each other, to form new kinds of molecules. This is a chemical change.

Again, zinc is sometimes said to *dissolve* in dilute sulfuric acid; but it is better to say that it *reacts* with the acid, since new materials are produced (§ 71), and it is impossible to recover the zinc as zinc, merely by evaporating the solution that is formed.

When two or more materials react in such a way as to produce but a single new material, they are said to **combine**; or to enter into a **chemical union** with each other. Thus charcoal may combine with the oxygen of the air to form carbon dioxide gas; and when plaster of Paris is mixed with water, the chemical union of the two results in a hardened mass of a new material, distinct from either plaster or water. We then say that the plaster has set.

8. Ingredients and Constituents.—The different materials that are intermingled in any mixture or solution are called its **ingredients** or **components.** These may be present in **varying proportions,** with a corresponding variation in the properties of the product. The sweetness of confectionery varies with its content of sugar; and the hardness of steel with its content of carbon.

On the contrary, the materials that have **chemically combined** to form any given product are called its **constituents.** It is possible to combine them only in **constant proportions**—a definite weight of one constituent for a definite weight of any other (§ 35). Thus when carbon is burned in a plentiful supply of air, one part by weight of carbon always combines with exactly two and two-thirds parts by weight of oxygen, to form carbon dioxide. If oxygen is supplied in excess of this amount, the excess is left over, uncombined. Since the constituents entering into any given chemical union always combine in a constant ratio, the product naturally has **constant and invariable properties.** Pure water, for example, at atmospheric pressure, always freezes at a definite temperature; and a given quantity of it, at any particular temperature, will always dissolve a definite amount of sugar or common salt. Mixtures, on the other hand, have variable properties, depending on the proportions in which their components are present.

9. Substances.—Most materials, as we meet them in nature, are readily recognized as mixtures or solutions, from their somewhat inconstant properties, and especially from their inconstant **chemical composition.** By this we mean that their ingredients may vary somewhat in their nature or amount. Glass, for example, contains variable amounts of its three chief ingredients (§ 411); and certain special glasses, like that used for telescopes, contain ingredients quite unknown in ordinary glass (§ 412). All the physical properties of glass—its relative heaviness, hardness, color, and softening temperature—vary with its varying composition.

Other materials, on the contrary, on being carefully purified, come at last to have a constant chemical composition and definite properties. Thus pure water is always composed of 1.008 parts of hydrogen in chemical union with 8 parts of oxygen—proportions that never vary in the least. Materials of constant chemical composition and definite properties are called **substances.** Other examples are sugar, common salt, sulfuric acid, sulfur, and iron. Their constant composition and definite properties are presumed to mean that **the molecules of any given pure substance are either all of the same kind; or at least** (if they are of different kinds) **are always intermingled in a constant ratio, when examined under given conditions.** Thus water, although a pure substance, is believed to consist of several kinds of molecules (§ 41), whose average character determines the properties of water in bulk. But these properties are nevertheless quite definite, because the different kinds of molecules, under given conditions, are always present in a constant ratio—a definite number of one kind for a definite number of every other.

10. How Substances are Purified.—We have just emphasized that materials commonly need to be purified before they acquire the constant chemical composition and definite properties that are characteristic of substances. This is because they are nearly always intermingled, as we meet them in nature, with noteworthy quantities of other materials, which we regard as accidental **impurities.** River water contains muddy material as an impurity, which may be removed by filtering; dissolved impurities then remain, which may be removed by being left behind when the water is distilled; but even distilled water contains noteworthy quantities of dissolved air, and often traces of material acquired from the walls of the container.

The properties of a substance or material are sometimes very seriously modified by the presence of impurities. Copper that contains a few hundredths of a per cent of arsenic is practically valueless as a conductor of electricity. It follows that any material whose properties are to be studied must first be suitably purified. This often calls for a high degree of skill and patience. Chemists frequently spend months or years in painstaking purification of materials to be used in their researches.

It will be interesting to consider some of the principal methods that chemists employ in purifying materials:

1. **Sifting.**—If the intermingled substances occur in particles of distinct sizes, a sieve may be used to separate them.

2. **Filtration.**—If a solid fails to dissolve in a liquid, it may nevertheless be so finely divided that it fails to settle out immediately when the two are shaken together. The mixture of solid and liquid is then called a **suspension.** If a liquid contains suspended impurities, these may often be removed by filtration. Read § 81.

3. **Evaporation and Drying.**—Read § 86.

4. **Magnetic separation.**—Iron and magnetic iron oxide may often be separated from other materials by means of a magnet.

5. **Froth flotation.**—Read § 529.

6. **Fractional distillation.**—Read § 83.

7. **Fractional crystallization.**—Read § 97.

Sometimes a material is more readily purified if one or both of its ingredients are first chemically transformed. Gold may often be purified by treating it with nitric acid, which reacts with other metals that may be present, forming soluble products, and leaving the gold unchanged.

11. Elementary and Compound Substances.—To **decompose** a substance is to produce from it two or more new ones, each weighing less than the original substance, and differing from it and from each other in chemical properties. Thus when sugar is strongly heated, it is decomposed into water vapor, various other gases and vapors, and a black residue, which is largely carbon.

Substances easily decomposed are said to be **unstable.** A sample of nitrogen triiodide (a gray-black powder) is so unstable that it will explode violently if touched with a feather. Other substances, comparatively difficult to decompose, are said to be **stable.** But among the hundreds of thousands of pure substances known are about ninety that are very much more stable than the rest.* We call these **simple** or **elementary substances.** They are listed on the front cover.

Since modern chemistry came into existence, about a century and a half ago, chemical investigators have made repeated and desperate attempts to decompose these elementary substances, but until recently without success. Concentrated sunlight, the intense heat of an electric arc, long contact with the most active chemical reagents, all fail. **Most elementary substances have never been decomposed at all.** Only within the past few years (since 1920) have a few of them been decomposed, mere traces in any one experiment, by means that are incomparably more violent than those needed to decompose non-elementary substances.

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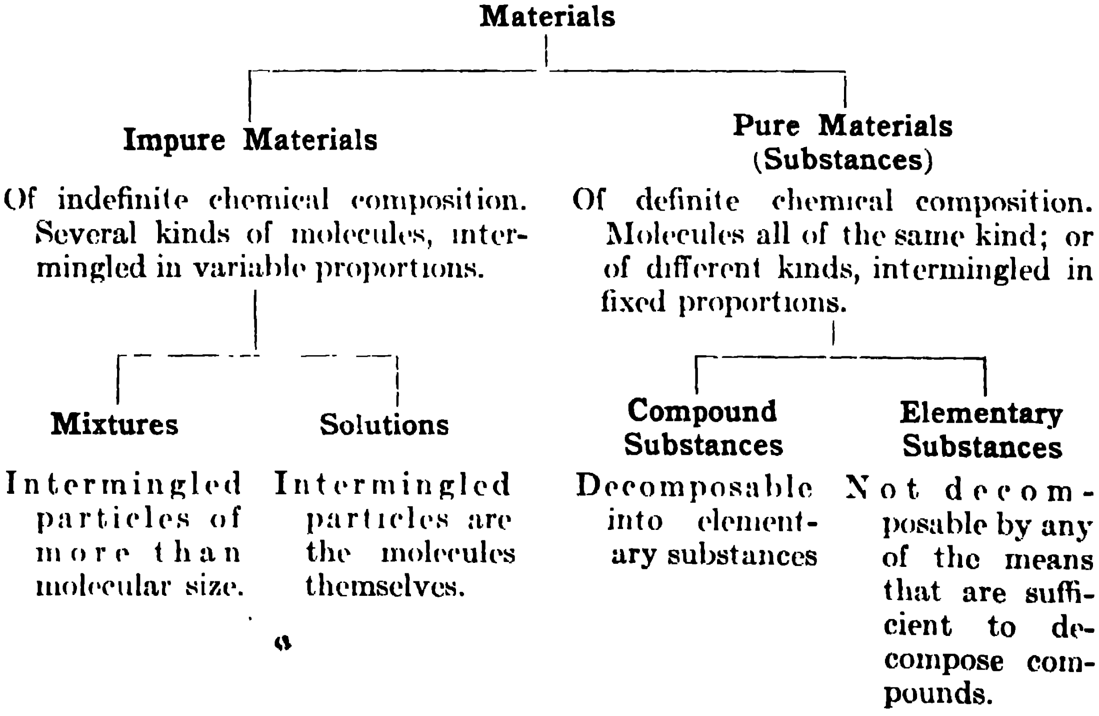
* At least toward *human* attempts to decompose them. For a few of them do decompose of their own accord, at a steady rate which is quite beyond human control (§ 600).

Conversely, **no elementary substance has ever been prepared by combining others.** Substances that may be prepared from, or that may be resolved into, elementary substances are called **compound substances, chemical compounds,** or simply **compounds.** Thus limestone is a compound, for it may be decomposed into quicklime and carbon dioxide gas; and these in their turn into the elementary substances, calcium, oxygen, and carbon. We have noted (§ 8) that substances always combine chemically in invariable proportions by weight. It follows that **every chemical compound contains definite percentages of its constituent elementary substances.** Water contains 11.19 per cent hydrogen, and 88.81 per cent oxygen, no matter how prepared.



Materials

Impure Materials

Of indefinite chemical composition. Several kinds of molecules, intermingled in variable proportions.

Mixtures

Intermingled particles of more than molecular size.

Solutions

Intermingled particles are the molecules themselves.

Pure Materials (Substances)

Of definite chemical composition. Molecules all of the same kind; or of different kinds, intermingled in fixed proportions.

Compound Substances

Decomposable into elementary substances

Elementary Substances

Not decomposable by any of the means that are sufficient to decompose compounds.

12. Elements.—An **element** is an elementary substance, existing either as such, or in chemical union with others as a constituent of a compound. Thus we speak of water as containing the two elements, hydrogen and oxygen, though these are not present in water in the elementary form at all, but in chemical union with each other. And when we speak of copper, we may mean either the familiar elementary substance, as we see it in a coil of copper wire; or copper after it has had all of its properties altered, by being combined with other elements, in a crystal of copper sulfate.

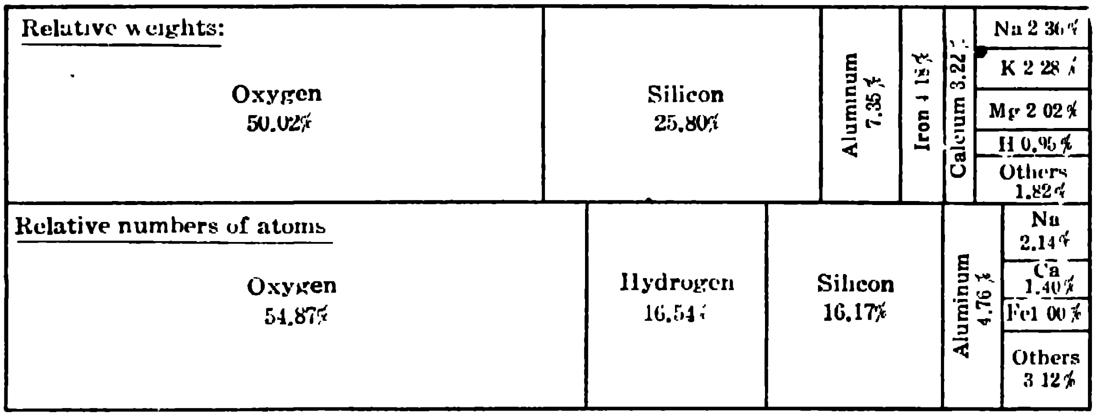


FIG. 1.—Composition of the Earth's Crust, Including Ocean and Atmosphere.

The known elements, about ninety in number, vary greatly in their relative abundance. Oxygen makes up about half of the weight of the solid rocks of the globe, eight-ninths of the ocean, and about a fifth of the atmosphere. Silicon comes next, which exists in combination with oxygen as quartz (white sand), and is an important constituent of many other minerals. Altogether it appears to be about half as plentiful as oxygen. If to these two elements we now add the six most common metals—aluminum, iron, calcium, sodium, potassium, and magnesium—we have 97 per cent of the crust of the earth, including the atmosphere, ocean, soil, and the solid rocks that happen to lie at depths not too great to be investigated. The other elements, about eighty in number, make up the remaining 3 per cent.

13. Atoms.—When we decompose a compound into simpler compounds than itself or, eventually, into its elements, we note that all its properties are altered. Thus we conclude that in decomposing a compound we decompose its very molecules, resolving these into particles of a still smaller size—as grains of wheat may be resolved into bran, middlings, and white flour.

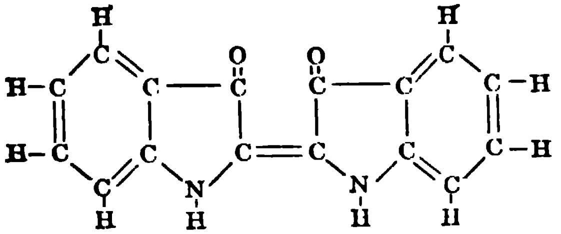
But by decomposing a compound we finally obtain elements.

These withstand further similar attempts to decompose them. Thus we conclude that molecules cannot be decomposed without limit, but must be composed of still smaller particles, which withstand all the efforts that are successful in decomposing molecules. We call these **atoms.** Thus practically all of the numberless chemical changes in the world about us are accomplished by rearranging atoms within molecules, or by separating them from each other and then recombining them into new molecules—as one might demolish a building and then bring the individual bricks and blocks of stone into new groupings, to construct another.

For example, when carbon is burned in a plentiful supply of air, we think of the process as consisting of the union of atoms of carbon with atoms or molecules of the oxygen of the air, to form molecules of carbon dioxide. When sugar ferments, we think of the molecules of sugar as being broken up, and their constituent atoms (of carbon, hydrogen, and oxygen) as being combined in a different way, to form molecules of alcohol and carbon dioxide.

This puts us in a position to answer the question (§ 1) whether it is possible to transform any given kind of matter into any other. At present, *no.* The first kind of matter must contain all the varieties of atoms that go into the making of the second kind. That is why we cannot turn lead into gold. But there still remains the possibility that we may one day be able to transform any given kind of atom into any other kind. The physicists and chemists of to-day are just beginning to consider means for accomplishing that; and recent success in decomposing a few elements (that is, *atoms*) shows that the feat of transforming one element into another, or one kind of atom into another, may not remain forever impossible.

We now know, not only how many atoms of each kind are contained in each given kind of molecule; but also, in part, how the atoms are arranged within the molecule with respect to each other. Thus we know that a molecule of helium—a rare gas now being used for filling balloons—consists of but a single atom. Atom and molecule, in this unusual case, are identical. But a molecule of oxygen is known to consist of two atoms. Separate these from each other and we get something that is no longer oxygen, in the ordinary sense. Again, a molecule of water consists of two atoms of hydrogen, combined with one atom of oxygen. Finally, a molecule of indigo contains many atoms of carbon, hydrogen, nitrogen, and oxygen, arranged in an invariable way with respect to each other, according to what we might call a definite "architectural plan."



Structural formula of indigo

FIG. 2.—Arrangement of Atoms in a Molecule of Indigo, C = carbon, N = nitrogen, O = Oxygen, H = hydrogen.

Some of the most complicated molecules whose structure is known to us contain several hundred atoms; and others, on incomplete evidence, are believed to contain thousands. Modern chemistry is founded on the assumption, not only that atoms and molecules exist, but that it is possible for us to learn their actual and relative weights and sizes, and the arrangement of atoms within molecules of the most complex kinds. But how we discovered all this we must leave for later chapters to disclose.

14. Some Suggestions on What and How to Study.— Though chemistry is a very interesting study, it is not always considered easy. Still, the difficulties of those who do have difficulties may generally be traced to improper methods of study. They may delay getting started until the rest of the class are hopelessly in the lead. Or they may imagine that they enter the course with sufficient knowledge to skip such preliminaries as are presented in the first few chapters. But since these chapters are concerned with laying the foundations, and with explaining the meaning of some terms which we must learn to use, it is not surprising that those who neglect them may thereafter find nothing clear or easy.

Your purpose in this course may be very simply stated: **To learn enough about the properties of a few common types of matter, and enough about the principles that govern the transformations of matter, to enable you to reason correctly about the chemical events of your daily life.** More particularly, we want you to acquire what might be called "the gift of chemical prophecy"— the ability to predict in advance, when familiar materials are to be brought together, what sort of new materials are likely to be produced, how these may be identified, and how separated from each other. We aim to cultivate, not memory, but reason.

Unfortunately, one cannot reason chemically, or in any other way, without a supply of individual facts on which to base his reasoning. The facts on which chemical reasoning is based are mostly facts concerning *properties*. In learning these, avoid the bookish point of view that you might employ in a course in history, in learning a list of battles or kings. Try to think what each actual substance looked like when you saw it in the laboratory, and what happened—what you saw, smelt, or heard—when you mixed it with something else. Especially try to remember what properties are possessed by whole groups of substances. When you get to Chapter X, try to catch its spirit, and the rest will be easy.

In studying the text, pause at the end of each of the numbered sections and try to recall what you have read. Better yet, draw up several questions, which you may put to some friend (or to yourself, the following week) to determine whether he knows the substance of that section. Be sure to pause to answer *all* the questions in small type in the body of the text, as you come to them (see p. 41). These will serve to show whether you really understand what you are reading. You will find answers at the close of the book.

The instructor will probably assign you a part of the exercises at the end of each chapter. But there is no rule to prevent you from working more than he assigns.

Reference: Pamphlet on "How to Study," Kornhauser (University of Chicago Press).

EXERCISES

1. Underline the particular words that should be used in the following sentences, and be prepared to defend your choice:

a. If a gas-jet is opened the escaping gas will (mix, combine) with the air; on lighting the gas it will (mix with, combine with, dissolve in) the oxygen of the air.

b. Water is freed from (dissolved, suspended) impurities by filtration; but (distillation, evaporation, drying) often removes both dissolved and suspended impurities.

c. Honey is a (mixture, solution, compound) which contains the following (elements, compounds, constituents, ingredients) among others: water, invert sugar, wax, pollen grains.

d. Sugar (melts, dissolves, reacts, combines) when placed in water.

2. By which of the methods of purification listed in § 10 would you attempt to purify:

a. Carbon disulfide (a volatile liquid, § 337) containing dissolved sulfur.

b. A substance fairly soluble in water, containing an impurity more readily soluble still.

c. A mixture of two solids, insoluble in water, and differing greatly in density (§ 89).

d. A mixture of two solids, one very soluble, the other slightly soluble.

3. The following are all mentioned in this chapter? Which are compounds, which elements, and which mixtures or solutions? Why?

Water, coal, glass, plaster of Paris, quartz, sulfur, limestone, air (§ 280), sugar, carbon dioxide, copper sulfate, steel, iron, calcium, quicklime.

4. From current advertisements, do you consider soap to be a compound or a mixture, and why?

5. Give several physical changes familiar to you, other than those mentioned in the text. Several chemical changes.

6. This book gives no formal definitions. But every technical word, where it first appears, is given in bold-faced type, with sufficient explanation to make its meaning plain. At the end of each chapter the student should go back to its beginning, and write out a definition, in his own words, of each of the terms thus indicated. A recent dictionary, or a reference text (Appendix K) may give suggestions; but the dictionary cannot be depended upon to give the particular sense wanted here.

7. Write paragraphs, explaining what difference in meaning exists between the following.

Material, object.
Descriptive chemistry, analytical chemistry.
Properties of materials, attributes of objects.
Physical properties, chemical properties.
Physical change, chemical change.

8. Similarly for the following:

Mixing, combining.
Dissolving, reacting.
Mixture, solution.
Ingredient, constituent.
Material, substance.

9. And for the following:

Molecule, atom.
Transform, decompose.
Suspension, solution
Elementary substance, chemical compound.
Chemistry, physics (§ 15)

CHAPTER II

THE THREE STATES OF MATTER

The material of this chapter may be introduced at any convenient point, previous to Chapter XII.

15. Physics and Chemistry.—Chemistry, in its study of the properties of matter, is supplemented by physics. We have already noted that physics is concerned with such properties of a material as may be studied without causing it to be transformed into materials of other kinds. Chemistry, on the contrary, seeks to determine the *conditions* or the *possibility* of transforming each given material into others. Thus when we remark that all gases expand when heated, and that all metals conduct electricity, we are stating facts of physics; but when we say that paper will burn, while asbestos will not, that is chemistry.

Now the transformations of matter that are the chief concern of chemistry (that is, *chemical changes*) are considered as being accomplished by rearranging or recombining atoms within molecules, to form molecules of other kinds (§ 13). Accordingly, it is sometimes stated that physics is chiefly concerned with such changes of matter as may be accomplished by rearranging molecules, or particles larger than molecules, with respect to each other; whereas chemistry is concerned with changes that take place within molecules to produce molecules of other kinds. This is roughly true. Yet one of the special provinces of physics is the study of the inner architecture of *atoms;* and of the changes that occur within atoms, in the few instances in which atoms have been decomposed, or have been observed to decompose of their own accord.

We should note that **all chemical properties are merely inferred from physical properties.** When we say that carbon burns to form carbon dioxide we are stating an inference. What we really observe is that a material having the physical properties of carbon disappears, and that another having the physical properties of carbon dioxide appears. Again, it is only by altering the physical surroundings of a given material that we can make it enter into a chemical transformation. Coal has to be heated before it will yield coal gas; and dynamite has to be subjected to the action of a detonating cap before it will explode.

Thus we see that some knowledge of physics is necessary to make even a beginning in chemistry; and a little physics is bound to get into every chemical textbook. No one who is preparing for a chemical career should fail to pass through several thorough courses in physics. The present chapter deals with the characteristics of the three **physical states**—solid, liquid, and gaseous—in which chemical substances may appear; for changes in state very often take place in chemical reactions. Thus two gases may react to produce a solid (§ 231—item 2); or a liquid may be decomposed to produce two gases (§ 65).

16. Scientific Laws.—All the natural sciences are alike in seeking to arrange and classify observations in such a way as to establish general principles or **scientific laws.** In science, a law is a concise general statement of what we believe to be an invariable method of behavior. We have already met with an instance. For we stated it as a law (§ 8) that whenever substances react chemically they do so in constant proportions—a definite weight of one for a definite weight of any other.

Sometimes such generalizations are called *natural laws,* as if they existed ready-formed in Nature, and man had only to find them out. On the contrary, Nature merely supplies us with individual objects and occurrences to observe. When we have made a certain number of observations, we make bold to draw conclusions concerning what we *believe* to be her invariable mode of behavior. But in so far as our observations are always limited in number, and confined to a definite interval of time and space—since our judgment, moreover, is subject to error—it is not surprising that our so-called natural laws must frequently be modified.

Nevertheless—and this should be emphasized—*a generally accepted law is rarely shown to be completely false.* It merely proves to be an *incomplete* or *slightly inaccurate* expression of what newer observations persuade us to regard as true. Thus, ultimate truth, if there is such a thing, is approached by science through a series of approximations.

17. Scientific Explanations. Theories.—But a bald statement that things always happen thus and so is sure to raise the query, *why?* Every scientific law calls for an *explanation.* In searching for this we very often discover that the law we are attempting to explain is merely a special case of some broader principle. But, in the end, a scientific explanation always takes the form of a *detailed description* of the thing we are attempting to explain. We *describe* a given process as taking place in a number of successive steps, leading to an observed invariable result; or we *describe* matter as consisting of small particles called molecules, having properties which, so far as we can see, would compel matter to behave as it does. Or we *describe* heat as consisting in the motion of molecules, and thus find it easier to understand why all other forms of energy tend to take the form of heat (§ 18), or we *describe* electricity as existing in small individual negative charges called electrons, which we conceive of as possessing properties that account for electrical phenomena in general.

Whenever such a detailed description of scientific facts has been so well worked out and so widely applied as to deserve special consideration, it is called a **scientific theory.** Science thus makes progress in two directions: first, by the systematic accumulation of facts, which it generalizes as scientific laws; second, by the development of theories that describe, relate, and thus in a sense explain the laws.

As individual facts are given a generalized expression in laws, so individual laws are related to each other, and find common explanation in theories. One who has never studied chemistry may know hundreds of isolated chemical facts, for most of the objects and events of our daily lives are matters of chemistry. The professional chemist, however, relies chiefly on a few dozen laws, from which he draws conclusions concerning a multitude of facts, individually unknown or unremembered. But only one who understands the general outlines and detailed implications of some half dozen great theories can be said to have mastered chemistry as a science.

In Greek, *theoria* means insight; and thus theoretical views are those that enable us to look beneath the surface of things to get at their real inner nature. Theories, when properly understood, are accordingly the most *practically useful* information one can possess. For (1) by connecting each law with a general point of view they help us to remember it; (2) they make plain the relationship to each other, and thus the deeper meaning, of laws which, standing alone, would not be properly understood; (3) they suggest new directions in which discoveries are likely to be made. For scientific discoveries are not made by chance, but are the result of systematic search for new facts and laws, guided by the intelligent use of theories. This is **scientific research.**

18. Energy.—A body in motion possesses what is called **kinetic energy,** *or energy of motion. The amount of this may be measured* (1) by noting the force that needs to be applied (as through the brakes of an automobile) in order to bring the moving body to rest *within a given distance;* or (2) by noting the distance that it will continue to move *after a given retarding force has been applied.* An automobile traveling forty miles an hour will remain in motion *four times as long* as one traveling ten miles an hour, after a given force has been applied through the brakes, and during this time will be traveling at an average rate *four times as fast.* Altogether then, it will go sixteen times as far, before being brought to rest. Thus we see that kinetic energy is proportional to the *square* of the velocity.

Energy in general is anything that may be made to take the form of kinetic energy. Heat is energy, for when released under a locomotive boiler, by burning coal, it may set a train in motion. Other forms of energy are light, electricity, the elastic energy of a coiled watch-spring, the surface-energy of a soap bubble, the chemical energy of a stick of dynamite, or the energy of position (potential energy) of a boulder on a mountain top.

In the processes occurring in nature, all the other forms of energy tend in the end to be dissipated as heat. This is presumed to indicate that heat energy (sometimes called **thermal energy**) consists in the energy of motion of molecules. In a hot body these are in violent agitation. In a cold one they are moving less energetically. But all other forms of energy, and all other forms of motion, tend to be dissipated as heat, because the motion tends to be transferred to the individual molecules of which all materials are composed.

19. Temperature Scales.—If heat is energy possessed by moving molecules, it follows that the quantity of heat in any body is determined both by the nature and number of its molecules and by their average individual energy of motion. This **average individual energy of molecules is** the measure of **temperature,** which is the quality that determines *the direction of transfer of* heat between one body and another.

The temperatures at which water freezes and boils, when the barometer stands at the standard height of 76 cm.* are taken as standard temperatures or **fixed points** on the principal thermometric scales.

In the **Fahrenheit** scale (° F.) the freezing point of water is arbitrarily taken as 32°, and its boiling point as 212°.

In the **Centigrade** scale (° C.) the same two points are called 0° and 100°. "Room temperature" means about 20° C.

Still another temperature scale, called the **Absolute** scale, is in common use in scientific work. In this there are 100° between the two principal fixed points, as in the Centigrade scale; but the freezing point of water is called 273° and the boiling point 373°.

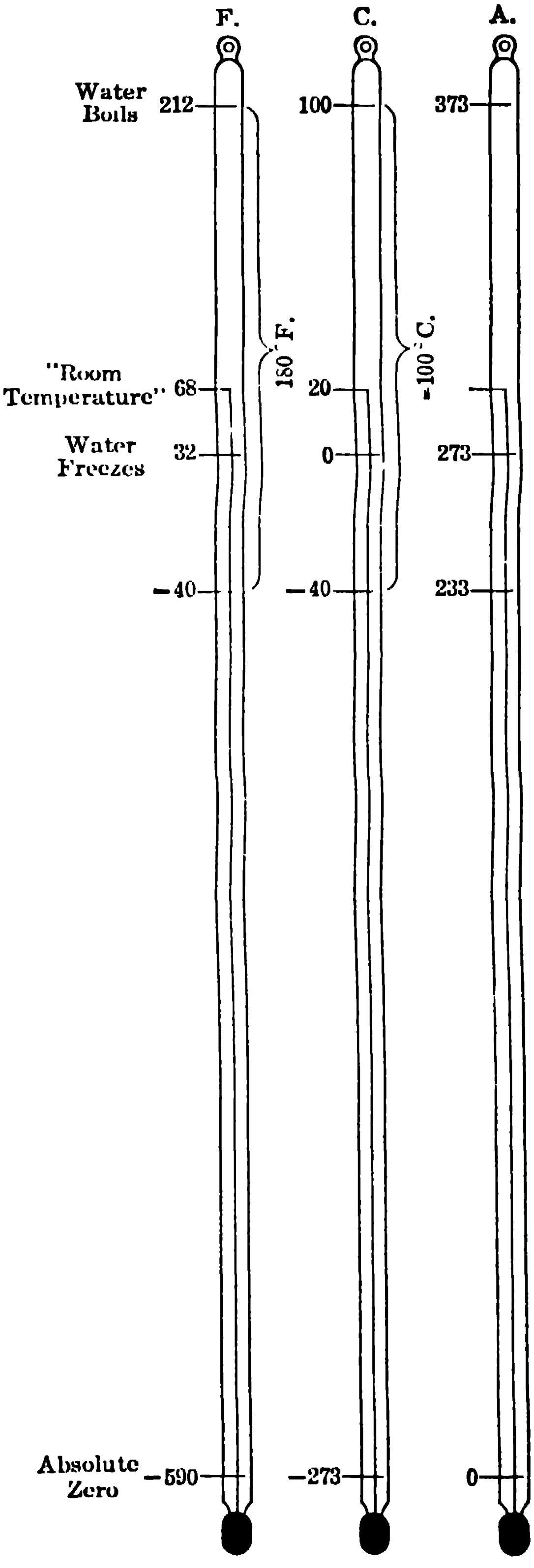


FIG. Temperature Scales.

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* Metric units are explained in § 33.

To convert centigrade degrees into absolute degrees, add 273. Thus −50° C. = 223° A.

One may occasionally need to convert Fahrenheit degrees into centigrade degrees; subtract 32, and multiply by $\frac{5}{9}$. Thus 68° F. = 20° C.

20. Characteristics of the Gaseous State of Matter.—Gases are distinguished from liquids and solids by their much lower density * and by the fact that they fill completely any vessel in which they are placed. A sample of gas thus has *no definite volume* and *no definite surface*, other than those of the containing vessel. Its volume depends on the external pressure, by means of which it is confined; and on the temperature.

Since gases are often invisible, and are so light that it is difficult to weigh them accurately, they are somewhat unpromising materials as objects of study. Still, they do have the advantage that they represent the simplest state of matter, and the one therefore that reveals the simplest laws. It is doubtful whether we would have any science of chemistry to-day, had not the founders of chemistry, a century and more ago, devoted much of their attention to the behavior of gases. As for the difficulty in weighing gases, that need no longer trouble us, for their considerable volume enables us to *measure* them accurately, and from their measured volume, at a definitely known temperature and pressure, it is easy to calculate their weight.

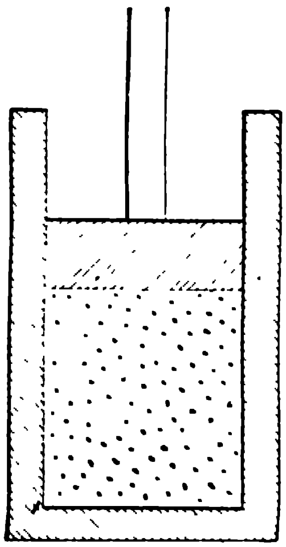

Fig. 4.

If a quantity of gas is confined within a cylinder fitted with a gas-tight, movable piston (Fig. 4), any increase in pressure will cause the piston to descend, and confine the gas within a proportionately smaller volume. For example, if the pressure is multiplied by five, the volume of the gas will be reduced to very nearly one-fifth, provided the temperature is kept constant. Thus, **at constant temperature, the volume of any gas is very nearly inversely proportional to the pressure upon it.** This is the **Law of Boyle.**

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* Density is the weight of unit volume.

If the pressure on the piston remains constant, while the temperature is increased, the gas will expand, and drive the piston outward. Raising the temperature from 300° A. to 600° A. will almost exactly double the volume. In other words, **at constant pressure, the volume of any gas is very nearly directly proportional to the absolute temperature.** This is the **Law of Charles.**

It should be noted that the laws of Boyle and Charles express only approximately the behavior of gases with changing pressure and temperature. At ordinary temperatures and under moderate or very small pressures, all gases (except hydrogen, helium, and argon) are somewhat *more* compressible than the Law of Boyle would indicate. With gases that are hard to liquefy (air, oxygen, hydrogen, nitrogen) the changes in volume at ordinary temperatures and pressures exceed those calculated by only a few tenths of 1 per cent. With the more readily condensible gases (carbon dioxide, sulfur dioxide, ammonia) the discrepancy may amount to several per cent. But all *highly compressed* gases, are much *less* compressible than the law of Boyle would predict.

All gases come more and more nearly into agreement with the laws of Charles and Boyle as the temperature is raised or the pressure is lowered. Thus all gases, as they become more and more highly rarefied, approach the condition of an **ideal** or **perfect gas** for which the two laws would hold exactly. The laws of Charles and Boyle are two of a group of ideal gas laws (others in §§ 22, 74).

§§ 152, 153 may be introduced here if desired.

21. The Molecular Theory of Gases.—The molecular theory makes four chief assumptions with respect to gases:

1. **The molecules of a gas move rapidly in straight lines, throughout all the space that it occupies, in all conceivable directions, with all conceivable velocities.**

2. **Most of this space is presumed to be empty, the diameter of a molecule being but a small fraction of its average distance from neighboring molecules.** Accordingly, each molecule can travel a considerable distance on the average before it meets with another molecule. But whenever two molecules do happen to collide they rebound without loss of energy.

3. **The molecules are assumed to be so numerous that their bombardment of the walls of the containing vessel sets up what**

seems to be a continuous pressure—just as a jet of water, sprayed from a garden hose in individual droplets, may press back a mass of shrubbery.

4. **A hot gas is assumed to differ from a cold one merely in having molecules that move with greater average velocity.** Certain facts show that **the average kinetic energy of the individual molecules of a gas is proportional to the absolute temperature.** Furthermore, this average kinetic energy of individual molecules, at any given temperature, must be the same for one gas as for another; else a change in the average kinetic energy, and accordingly a change in temperature, would occur on mixing two gases. Actually this does not happen.

But if the average kinetic energy of the molecules, at each temperature, is independent of the nature of the gas, it follows that **light molecules move faster than heavy ones**—so much faster that they make up in velocity squared for what they lack in mass.

22. Avogadro's Principle. Consider equal volumes of two different gases, both at the same temperature, and under the same pressure. Since the *temperature* is the same, each individual molecule of the one gas must have the same *average kinetic energy* as an individual molecule of the other. But since both gases set up the same *pressure* by their bombardment of the containing walls, it may be shown that the *total kinetic energy* of the molecules of the one must be equal to the total kinetic energy of the molecules of the other.

Now equal kinetic energy for individual molecules and equal total kinetic energy of course demands *equal numbers of molecules.* Thus **equal volumes of all gases, under the same conditions of temperature and pressure, contain very nearly the same number of molecules.** This is **Avogadro's Principle** (first recognized in 1811).

Accordingly, a cubic centimeter measure will contain very nearly the same number of molecules of gas, under given conditions, no matter what gas we put into it. This may seem as strange as though one were to state that a bushel basket necessarily held as many potatoes as peas; for different kinds of molecules differ greatly in size and weight. The explanation is, of course, that the molecules fill but a trifle of the space occupied by the gas, and are in rapid motion. Heavy molecules move relatively slowly. Light molecules move more briskly, make up in velocity squared for what they lack in mass, and thus beat back their neighbors on all sides to the same average distance as they would be able to do if they were heavy.

Let us now compare the *weights* of equal volumes of two gases. We find that oxygen gas is sixteen times as heavy as hydrogen. Then, if the equal volumes contain equal numbers of molecules, each individual molecule of oxygen must be sixteen times as heavy as a molecule of hydrogen. In general, **the weights of equal volumes of two different gases, under given conditions, are in the same ratio as the weights of their individual molecules.**

A certain vessel holds 10 mg. of nitrogen; another, five times as large, holds 350 mg. of mercury vapor, under the same conditions. What is the ratio of the weights of individual molecules of nitrogen and mercury?

23. How the Molecular Theory Explains the Properties of Gases.—

Observed Facts	*Explanation*
Gas pressure.	Bombardment of walls by molecules.
Diffusibility (§ 25).	Molecules in rapid motion.
Compressibility.	Large spaces between molecules.
Liquefaction. Gases condense to form liquids, when compressed and cooled.	Molecules tend to cohere when closely packed, especially at low temperatures.
Increase of pressure or volume with increase of temperature (Charles' Law).	Molecules move more rapidly at higher temperatures.
Decrease of volume with increasing pressure (Boyle's Law).	Increased pressure confines molecules in proportionately smaller volume.
Gases are cooled but slightly by expanding into a vacuum (*Joule's Law*).	Molecules of a gas have but slight attraction for each other, or tendency to cling together. If such attraction did exist energy would be absorbed in overcoming it.
Deviations from laws of Charles and Boyle (§ 20).	Attraction or cohesion between molecules not altogether absent. Volume occupied by molecules not altogether negligible.
Each gas, in a mixture of gases, exerts the same pressure that it would if it occupied the whole space alone (Dalton's Law of Partial Pressures).	Molecules are so far apart that they move without interference from each other; and when they happen to collide, rebound without loss of energy.
The preceding facts, viewed in relation to the laws of energy.	A given volume, under given conditions, contains nearly the same number of molecules, for all gases. (Avogadro's Principle.)

24. How Fast Do Molecules Move?—The molecules that compose a confined volume of gas are moving at all possible velocities in all possible directions. Each molecule, furthermore, by collision with its neighbors, is having its direction and velocity of motion altered at every instant.

But among all the velocities which the gas molecules may possess at any given instant, there is a certain *average velocity.* This we are able to calculate from the pressure that the molecules set up by their bombardment of the containing walls— and that, strange to say, without knowing the actual number of molecules that are concerned in setting up that pressure. It turns out that the molecules of hydrogen gas, at room temperature, have an an average velocity of about *a mile a second.* This is a pretty swift pace; but it is not an unbelievable one, for it would take this average hydrogen molecule about three-quarters of an hour to cross the American Continent, while an electric signal can span the gap in an inappreciable fraction of a second.

Heavier molecules move more slowly. Thus, with oxygen, which is sixteen times as heavy as hydrogen, the molecules move only one-fourth as fast.

25. Mixing of Gases by Diffusion.—If a small, open test-tube, containing a few drops of bromine, is dropped to the bottom of a deep glass cylinder, the reddish vapors of bromine work their way upward and presently begin to escape from the top of the cylinder. *This is in direct opposition to gravity, for bromine vapor is more than five times as heavy as air.*

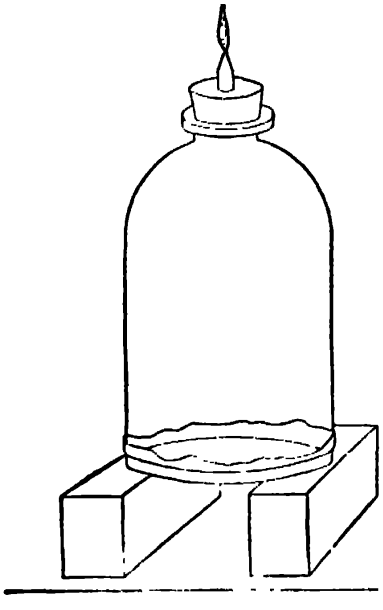

Fig. 5.

Again, if hydrogen is introduced through a tube at the top of a bell-jar supported above the table (Fig. 5) the air is driven downward by the lighter incoming gas, and escapes through a hole in a sheet of paper tied over the lower end of the jar. When the jar has been partly filled with hydrogen, the gas may be lit at the top of the tube through which it was introduced. It burns quietly for a few moments; but presently there is a fluttering, the flame strikes down through the tube, and the gas within the jar explodes violently, blowing off the paper drumhead. This experiment shows that hydrogen is so much lighter than air that it will remain above the latter for a little while, as oil remains above water, without complete mixing. But the final explosion shows that the two gases do mix to some extent in spite of their great difference in density, and that beneath the layer of pure hydrogen is one containing both hydrogen and air.

These experiments illustrate a general principle. **Whenever gases are placed in contact they will mix spontaneously in spite of differences of density.** This spontaneous mixing of gases, which have been placed in contact or which are separated by a porous wall, is called **diffusion.** The molecular theory easily accounts for it. The individual molecules of the two gases are in such rapid motion that gravity is no more effective in keeping them apart than it would be in preventing the mixing of two swarms of gnats.

26. Average Distance of "Free Flight" of Molecules.—But notice that the diffusion of gases in the preceding illustration does not take place at any such rate as would seem to be indicated by the molecular velocities given in § 24—a mile a second in the case of hydrogen. The reason is that no molecule can really go very far before it collides with another molecule and is turned back. Thus, a foreign gas or vapor, introduced into any part of the earth's atmosphere, will linger for a time near that particular spot. It was this circumstance that made gas shells effective during the Great War.

Calculations show that the molecules of most gases, at standard conditions, have an average free flight of only one sixty-thousandth of a centimeter.* That is *about as many halts in the distance of a centimeter as a man makes steps in walking thirty miles.* Yet the average hydrogen molecule travels 180,000 centimeters in a second, and gets as many knocks in that time and distance as a watch makes ticks in fifty years!

In a partial vacuum, the free flight of a molecule is very much increased, being in fact inversely proportional to the pressure under which the gas is confined. This fact is of practical interest in the manufacture of incandescent lights. It is necessary to pump the air out of these to prevent oxidation; but in a vacuum thus produced the filament "evaporates" rather rapidly and is deposited as a metallic film on the inner surface of the glass. The remedy is to fill the bulb with nitrogen or argon. Thus the average flight of the metallic molecules is very much reduced, and many of those that leave the filament are caused to return to its surface. Here we have an illustration of the chief lesson taught by the so-called theoretical sciences; that even the intensely practical-minded man can afford to follow truth a certain distance for its own sake, secure in the conviction that useful applications will not be long delayed.

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* A centimeter is about two-fifths of an inch.

27. Diffusion of Gases through Small Openings.— Diffusion acts to bring about the spontaneous mixing of gases, even though these may be separated by a porous wall.

Consider a wall containing a number of small openings, with hydrogen on one side and oxygen on the other. Now, if both gases have the same temperature and pressure, they will contain the same number of molecules in a given volume. This would seem to give both kinds of molecules an equally good chance of getting through the openings. But hydrogen molecules, being sixteen times as light as those of oxygen, move four times as rapidly (§ 24). Thus they arrive at the openings in the wall four times as often as oxygen molecules do, and pass through to the other side. And four times as many molecules (Avogadro's principle) means that four times as great a *volume* of hydrogen passes through the wall in any given interval of time. In general, **the relative volumes of two gases diffusing through a porous wall in a given interval of time, under the same conditions, are inversely proportional to the square roots of their densities.**[*] **This is the Law of Graham.** Note that it compares one gas with another, under the same conditions, *not* one gas with itself, under different conditions. Furthermore, note that diffusion is related to the velocity of molecules, and not at all to their size. All openings that we know anything about are so large in comparison with molecules that the latter have no trouble in passing through.

What volume of carbon dioxide gas, which is roughly 25 times as heavy as hydrogen, will diffuse through a porous wall in the same time as one cubic centimeter of hydrogen, under the same conditions?

Five cubic centimeters of a certain gas will pass through a porous wall in the same time as ten cubic centimeters of oxygen, under the same conditions. How does the density of the gas compare with that of oxygen?

The phenomenon of diffusion through porous material is commonly illustrated by means of the apparatus shown in Fig. 6. This consists of a cylinder of porous clay, the walls of which contain an immense number of microscopic openings. The cylinder is connected by glass tubing with a balloon-flask and a large beaker of water. When a bell-jar of hydrogen is lowered over the porous cylinder, hydrogen diffuses inward through the microscopic openings about four times as fast as air diffuses out. The pressure thus set up within the porous cylinder is relieved by air escaping through the beaker of water. But when the bell-jar of hydrogen is removed the reverse change takes place: hydrogen escapes through the pores of the cylinder faster than the air can enter, a partial vacuum is created, and a fountain of water from the beaker spurts up into the flask.

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[*] Density is the weight of unit volume. We are here dealing with relative densities, that is, the relative weights of equal volumes of different gases.

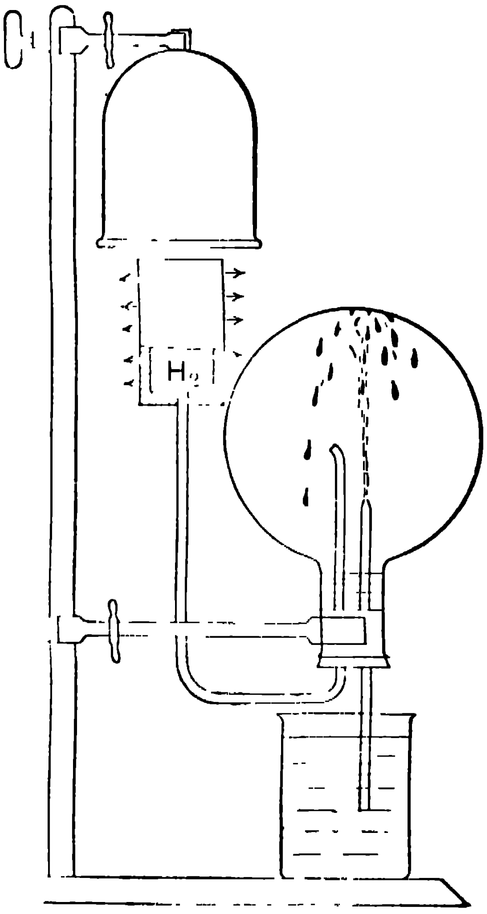

FIG. 6.—Diffusion of hydrogen through a porous cup.

28. The Molecular Condition of Liquids.

—A liquid differs from a gas in possessing a **definite volume** under given conditions, independent of that of the containing vessel. Liquids, volume for volume, are much heavier than gases, that is, have a greater **density.*** This indicates that comparatively little space exists between the molecules of liquid, and none of them can move very far before colliding with neighboring molecules.

We may reason that this smaller average distance between molecules of a liquid must permit them to exert a much greater average attraction for each other than do the molecules of a gas. The motion of molecules *within the interior* of a liquid should nevertheless be but slightly interfered with by this attraction, for the reason that it is a *balanced* attraction. Each given molecule must experience nearly the same pull in all directions, due to neighboring molecules.

But molecules *near the surface* of a liquid experience an *unbalanced* attraction. Their neighbors all tend to pull them downward—to drag them into the interior of the liquid, and thus diminish its surface. This tendency of a liquid to diminish its own surface is measured by what we call its **surface tension.** Its effects are roughly like those that might be produced if the surface of the liquid were covered by a stretched rubber membrane. That is why soap bubbles, or small droplets of liquid, tend to assume a spherical shape.

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* Though under very great pressures certain gases that are difficult to liquefy may possess a density comparable with that of liquids, and still remain in the gaseous condition.

As the temperature of a liquid is reduced, its molecules move more and more slowly, and are rolled over each other with increasing difficulty. The liquid thus increases in **viscosity,** and in some cases passes gradually and continuously through more and more viscous stages, until it finally becomes rigid, without any sudden change in properties at any particular temperature. Glass, for example, is not a true solid, but merely a highly viscous liquid, flowing under pressure, though more slowly than the proverbial "molasses in January." Sometimes such substances are called **supercooled liquids** or **amorphous solids** (Greek, *formless*).

29. Evaporation. Vapor Pressure. Aqueous Tension.—The molecules within the interior of a liquid have a definite average energy of motion, and thus a definite average velocity at each temperature. Some of them, however, at any given instant, have a velocity sufficiently greater than the average velocity to enable them to break through the surface layer of molecules and escape. Thereafter they are free to wander about in the space above (Fig. 7) and constitute a **vapor**—namely a gas that can be condensed to a liquid merely by increasing the pressure upon it. (Air is not a vapor, for to condense it to a liquid it must be both compressed and cooled.)

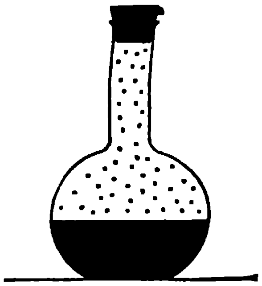

FIG. 7.

The escape of molecules from a liquid into its vapor is called **evaporation.** A liquid that evaporates readily is said to be **volatile.** After a sufficient number of molecules have collected in the space above the liquid, their haphazard wanderings bring them back to the surface as fast as other molecules escape. Thereafter, there is a balance between evaporation and recondensation and thus a *constant number* of molecules within the closed space at any given moment; and these, by bombardment of the walls of the vessel set up a constant pressure, called the **vapor pressure.** This depends on the *temperature* and on the *nature of the liquid,* but not at all on the amount of liquid. For when a certain pressure has been reached at each given temperature evaporation is exactly balanced by recondensation no matter how much liquid is present. The vapor pressure of water is sometimes called **aqueous tension.**

Vapor pressure may be demonstrated by drying a large bottle and fitting it with a stopper that carries a rubber-tipped medicine-dropper, such as is used for filling fountain pens, and a U-shaped gage containing some colored liquid (Fig. 8). We note the level at which the liquid stands in the outer arm of the gage, then introduce a few drops of a volatile liquid into the bottle by means of the dropper. Immediately the liquid in the gage begins to rise, showing that the evaporating liquid is producing a pressure.

Another way of demonstrating or measuring vapor pressure is to introduce a few drops of a volatile liquid into the vacuum above the mercury in a barometer. Some of the liquid will evaporate, and presently it will be found that the level of the mercury has been depressed by a definite amount, which depends on the temperature.

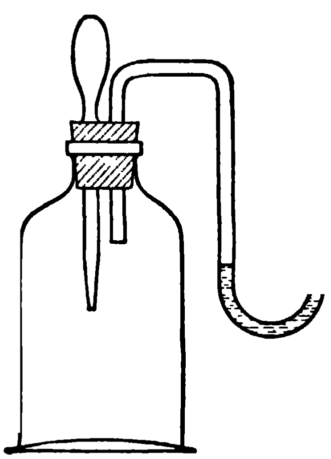

FIG. 8.

30: The Structure of Crystals.—A **true solid** or **crystalline solid** may easily be distinguished from an amorphous solid or supercooled liquid:

1. It tends to assume a **crystalline form** (*i.e.*, a definite geometrical shape, bounded by plane surfaces, and having special optical and mechanical properties not found in amorphous bodies).
2. It **melts at a definite temperature** (§ 85).
3. It **absorbs a definite amount of heat in melting** (§ 85).

We may assume that the regular geometrical form of a crystalline substance is due to a corresponding arrangement of its atoms or molecules - just as the regular outline of a regiment on parade betrays the regular arrangement of the individuals that compose it.

This view has had remarkable confirmation within the past few years. A beam of X-rays is passed through a narrow slit, then through fragments of a crystalline solid, such as powdered quartz sand, and is permitted to fall upon a photographic plate. An image is formed, consisting of a series of parallel streaks (**Fig. 9**). The explanation is that each atom of the crystalline powder absorbs, and reëmits, a portion of the energy of the X-ray beam.

Something similar may often be observed on a pond of water, when ripples traversing its surface, and arriving at a row of stones, are reflected as secondary ripples, in circles from each stone. Now since the atoms of the crystalline powder are regularly arranged, the energy which they reëmit produces a regular pattern on the photographic plate, and that in spite of the fact that the powder may be very finely ground, and disposed in the path of the rays in a haphazard manner.

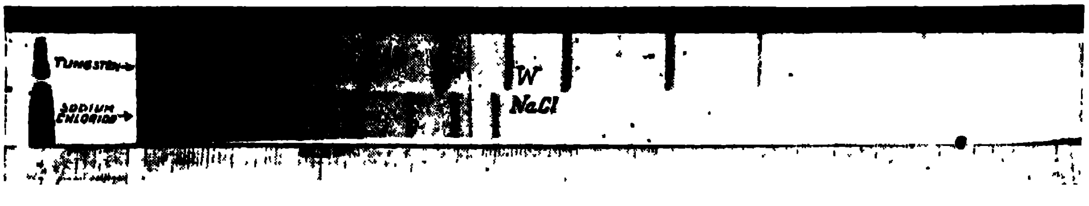

FIG. 9.—Images produced on a photographic plate by a beam of X-rays, after passing through crystalline powders.

From such X-ray photographs, physicists have been able to tell just how the atoms of each kind of crystal are arranged with respect to each other, and to construct models, such as those shown in Figs. 10 and 11, in which the different kinds of atoms are represented by spheres, occupying the corners of a lattice-work. It turns out that the units of crystal structure are commonly atoms, rather than molecules (Fig. 10); though occasionally cer-

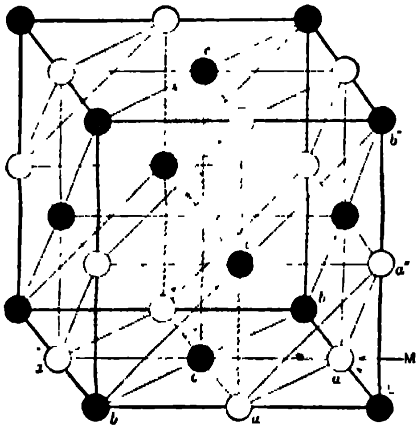

FIG. 10.—Arrangement of atoms in a crystal of common salt. Atoms of sodium (white circles) and chlorine (black circles) occupy alternate corners of cubical space lattice.

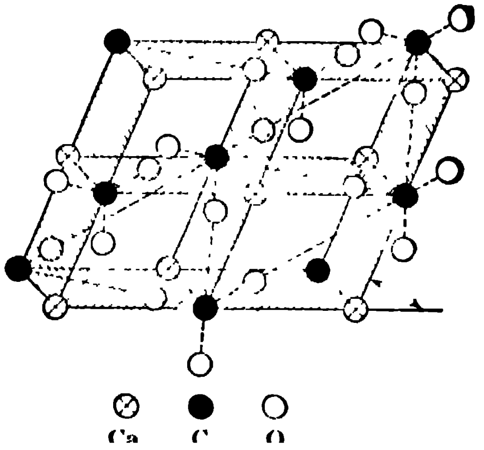

FIG. 11.—Arrangement of the atoms in a crystal of calcite ($CaCO_3$). Note that each carbon atom has three oxygen atoms, symmetrically disposed about it.

tain groups of atoms (Fig. 11) forming parts of molecules, maintain their identity even in the crystal.

31. Sizes, Weights and Numbers of Atoms and Molecules.—By studying matter in bulk, physicists have been able to draw conclusions concerning the sizes and weights of the individual atoms and molecules that compose it, and the number of these that are present in a given volume of gas or a given area of crystal surface.

Sizes of Molecules

Measurements of the rate of flow of gases through fine openings, of the thickness of oil films on water, and other methods, enable us to calculate the size of molecules. A molecule of oxygen, assumed spherical, proves to have a diameter of roughly 2.7×10^{-8} cm.* In more familiar language, *about one hundred million molecules of oxygen can be laid down side by side in a distance of 1 in.*

Number of Molecules in a Cubic Centimeter of Air

Methods to be mentioned in the next section permit us to calculate the number of molecules in a cubic centimeter of air—which is the same (§ 22) as the number contained in a cubic centimeter of any other gas—at standard conditions (§ 22). This turns out to be around 27×10^{18}—namely 27 followed by eighteen zeros. Otherwise expressed, there are as many molecules in a cubic centimeter of gas as grains of sand, each one-fiftieth of an inch in diameter, in a cubic mile of sand. But since the molecules of air are in motion, a better illustration of the number in this mere thimbleful of air would be a snowstorm. A fall of 27×10^{18} snowflakes would cover the the whole United States, three million square miles, to a depth of about an inch.†

Number of Atoms in a Crystal

When the arrangement of the atoms in a crystal has been determined by observations with X-rays (§ 30), a simple calculation, based on the density of the material, enables us to calculate the distance of each atom from its neighbors. This varies somewhat from crystal to crystal, but is around 2.8×10^{-8} cm., the figure for common salt. Otherwise expressed there are about 35,000,000 atoms of sodium and chlorine in a distance of 1 cm. (= 0.4 in.), measured along an edge of a crystal of common salt; and in the surface layer of a cubical crystal 1 cm. on an edge (Fig. 10) we would have the square of 35,000,000—more than as many atoms, in fact, than there would be bricks, of 32 sq. in. each, in a brick pavement covering the whole continent of North America.

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* 10^n means a figure *one*, followed by n zeros; 10^{-n} means a *one* in the nth decimal place, preceded by zeros. A centimeter (cm.) is about two-fifths of an inch (§ 33).

† Observations in several Nebraska snowstorms show that a large snowflake may weigh as much as 5 mg.

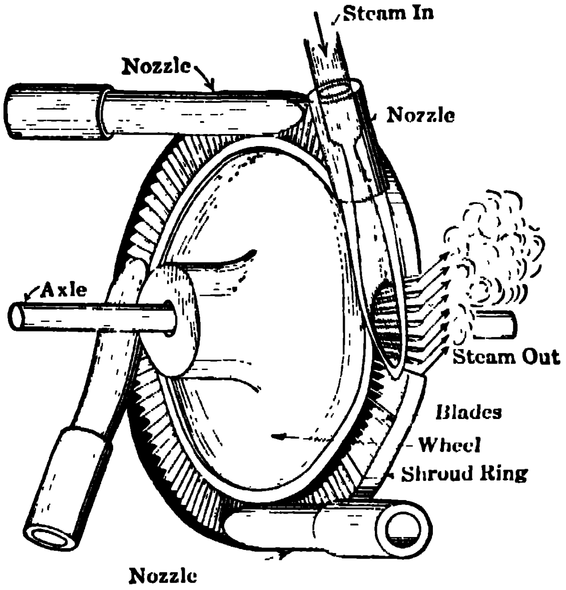

FIG. 12.—Principle of the steam turbine—a device for putting molecules to work. As the steam passes through the turbine a part of the energy of motion of its individual molecules is converted into mechanical energy. The average velocity of the molecules, and accordingly the temperature of the steam, is thus very much reduced.

32. Are Atoms and Molecules Real?—The atomic and molecular theories *furnish a reasonable* explanation of many facts otherwise rather hard to explain. It is conceivable, however, that an explanation may be in harmony with all facts now known, and at the same time be false. Is the atomic theory anything more than a convenient frame on which to hang our odds and ends of information concerning natural phenomena? *Are atoms and molecules real?*

In answer we ought to note that a molecule of water is not less real than a visible droplet, merely because it does not appeal directly to our senses. Who ever saw an X-ray or a wireless wave, or weighed and measured life. Every criminal tracked down by a detective agency bears witness to the fact that it is possible to prove a good many things by indirect evidence alone.

The practical man accepts things as real if their existence is indicated by several independent indications, provided such acceptance does not contradict previously accepted reality. Now, many kinds of evidence not only point to the existence of atoms and molecules but agree concerning their size, weight, number, distance apart, and velocity of motion. Thus, the number of molecules in a cubic centimeter of any gas at standard conditions (§ 31) has been deduced from such diverse sources as the rate of settling of a swarm of small particles suspended in water or air; the rate at which helium gas is formed from radium salts (§ 586, item 4); the movement of droplets of oil in an electric field; and the discharge of electricity through rarefied gases. All these agree within about 1 per cent. Again, calculations giving the size of molecules from the rate of flow of gases through fine openings are in harmony with the maximum diameter of atoms, as given by observations of crystals with X-rays.

We must, therefore, either accept atoms and molecules as being quite as real as the visible objects about us; or we must admit that we know nothing about reality, and that all things may be but the substance of dreams. But if they are real, and if all chemical changes are effected by rearranging and recombining them, then everything we can learn about them is apt to be of

EXERCISES

1. In what important respect are atoms different from molecules?
2. State several respects in which gases are all alike, and explain in terms of the molecular theory.
3. Outline the principal assumptions of the molecular theory of gases with respect (*a*) to motion of molecules; (*b*) relative space between molecules; (*c*) cause of the pressure set up by a gas; (*d*) conditions at absolute zero.
4. Upon what does vapor pressure depend? Distinguish between vapor pressure and aqueous tension. Why is vapor pressure independent of the *amount* of evaporating liquid?
5. How can you explain the fact, in terms of the molecular theory, that an increase of temperature results in an increase of vapor pressure?
6. Explain what would happen, and why, in the experiment of Fig. 6, if a gas heavier than air were used instead of hydrogen.
7. A liter of oxygen is found to be sixteen times as heavy as a liter of hydrogen. Compare the weights of the individual molecules. State the principle involved.
8. Describe the method by which it is possible to demonstrate the essential difference between true and amorphous solids.
9. What is wrong with the definition: "A crystal is a solid of definite geometrical shape, bounded by plane surfaces."

10. What properties distinguish a liquid from a gas? A true solid from a supercooled liquid?

11. The dark stain that sometimes accumulates on the inner surface of incandescent light bulbs is a deposit of metallic molybdenum, due to atoms of molybdenum which evaporate from the filament at high temperatures, and adhere wherever they happen to strike the walls. From the manner of formation of this deposit, tell whether it is probably amorphous or crystalline, and why. (The molybdenum is an impurity in the tungsten filament.)

12. Explain, in the language of the molecular theory, why automobile headlights are often nitrogen-filled.

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13. With the help of a dictionary, in comparison with the text, draw up definitions for the following terms, appearing in this chapter: Scientific law; scientific theory; scientific research; force; energy.

14. Similarly, define the following: Ideal gas; density; diffusion; vapor; evaporation.

15. Similarly, define: Vapor pressure; viscosity; surface tension; volatility; crystal.

16. State and illustrate the law or principle due to each of the following: Charles; Boyle; Graham; Avogadro.

17. Refer to the encyclopaedia for a few facts about the lives of these four men, including at least one other scientific achievement in the case of each.

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18. A balloon has ascended to a considerable height, and the decreased pressure has permitted the hydrogen to expand, until a large part of the gas has been lost. Will diffusion through the fabric of the balloon now take place more or less rapidly than before, and why? Explain whether the Law of Graham does or does not apply, and why.

19. Helium, volume for volume, is about one-fourth as heavy as ammonia. What volume of helium will diffuse in 15 seconds through a porous porcelain wall that will pass 1000 cubic inches of ammonia in one minute? State the law that applies.

20. A liter of hydrogen weighs .09 gram. What will be the weight of a liter of sulfur dioxide gas, under the same conditions if a molecule of sulfur dioxide is known to be thirty-two times as heavy as a molecule of hydrogen? State the principle involved.

21. What is the root-meaning of the word theory? Explain the practical use of theories.

22. If a gas occupies a volume of 100 cu. in at 27° C., what volume will it occupy at 127° C. (Change temperatures to absolute scale.)

23. To what temperature must a gas be heated, in order that its volume at −73° C. may be doubled?

24. A gas occupies a volume of 100 cu. in. under a pressure of 15 lbs. per sq. in. What pressure must be placed upon it to decrease its volume to 75 cu. in.?

CHAPTER III

WEIGHT RELATIONS IN CHEMICAL CHANGE

33. Metric Units.—Scientific work, the world over, is expressed in units of the metric system. These are definitely fixed, by international agreement, whereas those of the English system are often variously defined in various parts of the English-speaking world. Moreover, many units of scientific interest have never been defined at all in any other system than the metric. Finally, calculations in the metric system are very much simplified by the fact that different units measuring the same quantity are related as multiples of ten.

The student should commit to memory the approximate equivalents here given, with abbreviations. Look up the exact equivalents when needed.

Length:

1 millimeter (mm.) = about $\frac{1}{25}$ in. = about the thickness of 12 leaves of this book.
1 centimeter (cm.) = 10 mm. = about 0.4 in. (exactly, 0.3937 in.)
1 decimeter (dcm.) = 10 cm. = 100 mm. = about 4 in.
1 meter (m.) = 10 decimeters = 100 cm. = 1000 mm. = 39.37 inches, or a little over a yard.

Weight:

1 milligram (mg.) = smallest unit of weight in the metric system.
(A postage stamp weighs about 50 milligrams).
1 gram (g.) = 1000 mg. = 980.7 dynes = about $\frac{1}{28}$ oz., Avoirdupois.
(A new American 5-cent piece weighs 5 grams.)
1 kilogram (kg.) = 1000 g. = 1,000,000 mg. = 2.2+lbs. (exactly, 2.2046 lbs.)

Volume and Capacity:

1 cubic centimeter (cc.) = volume of a cube 1 cm. on an edge = volume of about 20 drops of water.
1 milliliter (ml.) = the volume occupied by 1 g. of water, weighed in a vacuum, at 4° C. This unit was intended to be—and *is*, within 0.0027 per cent—the same as the cubic centimeter.
1 liter (l.) = 1000 ml. = 1000 cc. = volume occupied by 1 kg. of water, in a vacuum, at 4° C. (exactly, 0.26417 U. S. gal.)

Temperature. § 19.

Heat. Appendix H.

34. The First Law of Chemical Change: Conservation of Weight.—Review §§ 7, 13. The different substances that react with each other in any given chemical change are called the **reactants.** These are transformed, and one or more new substances come into being, which are called the **resultants,** or the **reaction products.** Thus, when carbon burns in a plentiful supply of air, the reactants are carbon and oxygen (of the air), and the resultant is carbon dioxide.

Chemistry began to be a science when men first began to *weigh* the reactants entering into chemical changes, and to separate and *weigh* the resultants. Thus it was quickly discovered that **there is no detectible gain or loss of weight in any chemical reaction.**

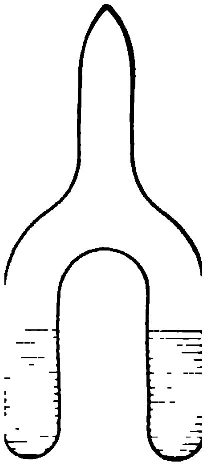

Fig. 13.

A simple demonstration of this law is shown in Fig. 13. Two different materials (commonly solutions) are placed in the two arms of the tube. The tube is next sealed off at the top, and weighed as accurately as possible. It is then shaken, to bring the reactants together; and after the chemical change has taken place the tube is permitted to cool, and is weighed again. This experiment has been carried through with chemical reactions of many different types, with very accurate balances, but no change in weight has ever been detected that exceeded the possible weighing (about one part in ten million).

Thus, however completely the reactants may have their properties altered, there is one property— their total weight—which remains unchanged. The sum of the weights of the reactants, as nearly as we can determine, is exactly equal to the sum of the weights of the resultants. This is the **Law of Conservation of Weight.** Since weight (at any one place) is assumed to be a measure of mass or quantity of matter, we sometimes restate this principle as the **Law of Conservation of Matter.**

35. The Second Law of Chemical Change. Definite Proportions.—Chemists have always been interested not merely in determining *what kinds* of substances are transformed or produced in chemical reactions, but *how much* of each. What relative weights of carbon and oxygen are needed to produce carbon dioxide? What weight of sugar must be fermented to produce a given weight of alcohol? Beginning with the work of Black, in England (1755), investigators devoted much effort, during half a century, to a study of such weight relations, gradually accumulating data sufficient to establish a second law governing chemical change. **Every chemical change transforms invariable relative weights of the reactants, to produce invariable relative weights of the resultants.** This is the **Law of Invariable Weight Relations or Definite Proportions.** Thus when alcohol is burned in a plentiful supply of air, every gram of alcohol combines with a definite weight (2.09 g.) of oxygen to produce a definite weight (1.91 g.) of carbon dioxide and a definite weight (1.18 g.) of water vapor. Every pound of red lead (a paint pigment) must contain a definite weight of lead; and each pound of copper arsenite insecticide must contain a definite weight of copper.

Show that the figures just quoted for the burning of alcohol also illustrate the law of Conservation of Weight.

How much alcohol must be burned if the carbon dioxide and water vapor together weigh 6.18 g.?

Reword the Law of Invariable Weight Relations to express what happens when two substances, A and B, react to produce two new substances, C and D.

The law just stated of course applies to the special case in which elements combine directly to form compounds. Thus **any given compound always contains the same elements in the same proportion by weight, no matter how prepared.** This special case of the Law of Definite Proportions is called the **Law of Constant Composition.** Note that this serves rather as a definition of chemical compounds than as a general law. We examine the different non-elementary materials found in nature or prepared artificially, and discover many among them that are *invariable* in their chemical composition. These we set apart in a group by themselves, and call chemical compounds. Other materials, of *variable* composition, we call mixtures or solutions.

Again, when we say that oxygen and hydrogen combine in invariable relative weights to form water we are not stating that it is impossible for these elements to combine in other proportions than those given. We merely mean that if they do the product will not be water.

36. Dalton's Principle.—The two laws just considered suggest certain properties of atoms. These, in their turn, explain the laws:

Laws	*Explanations*
1. There is no change in weight during chemical reactions.	1. The weights of individual atoms are not altered by combining them with each other.
2. All samples of a given compound contain the same elements, in the same proportion by weight.	2. All the molecules of a given compound contain invariable relative numbers of different kinds of atoms, each kind having a definite average weight.

Otherwise expressed, our explanations come to this: **The atoms of each given element have a definite and invariable *average* weight; and molecules are formed by combining definite whole numbers of atoms.** This may be called **Dalton's Principle,** since it was first stated (somewhat imperfectly) by John Dalton, an English schoolmaster, in 1808. (Not to be confused with Dalton's Law of Partial Pressures, §23.)

This implies that the atoms of any given element may all be of the same weight; but if they happen to be of different weights, they are always intermingled in such proportions as to have an invariable *average* weight. For example, the fact that tin combines in invariable proportions with other elements, regardless of its geographical source, shows that tin atoms possess an invariable *average* weight, whether they come from the mines of England, Bolivia, or Southeastern Asia. A sample of nickel from Australia consists of atoms of the same average weight as one from Canada. Thus it appears that the materials that compose our earth came into being by processes that everywhere produced the same average sorts of atoms; or that the components of the earth crust, at some early stage of the earth's history, got very thoroughly scrambled. Only in the case of some elements whose atoms are known to be of recent origin—recent, that is, as geology counts time— has the average weight of atoms of a given kind been found to vary with the source of the material.

37. Atomic Weights.—The relative weights, therefore, in which elements combine with each other are determined by the relative weights of their individual atoms. The manufacturer of red lead paint wants to make as much of this pigment as possible from each pound of metallic lead; and the farmer, purchasing copper arsenite insecticide, would be glad if this material contained a smaller percentage of the expensive metal copper. Yet both are the victims of Dalton's Principle—the atoms of lead and copper have pretty heavy average weights and we have got to pay accordingly. An alteration in the accepted values for the relative weights of these atoms affects our pocket-books just as surely as altered quotations on the market or an increased tariff. A keenly practical interest attaches to this matter of the relative weights of atoms.

The **average relative weight** of the atoms of any particular element, in comparison with an atom of oxygen (taken as sixteen units) is called its **atomic weight.** Thus when we say that the atomic weight of lead is 207.20, we mean that our best information shows that each atom of ordinary lead, on the average, weighs 207.20 times as much as a sixteenth part of an atom of oxygen. This is as if we were able to place a single atom of lead on one pan of a balance of less than microscopic size, and counterpoise it with minute weights placed upon the other pan—each of these weights being a sixteenth part of an atom of oxygen. (We use the sixteenth part of an oxygen atom for our unit, since the lightest known atom, that of hydrogen, then turns out to be very nearly one.)

Of course, no one has actually weighed individual atoms in any such fashion. They are far too small for that. Their relative weights have to be determined by indirect methods, and are indeed disclosed by the very facts that suggested Dalton's Principle—the proportions by weight in which elements combine when taken in quantities that are large enough to weigh. For if we assume that all the molecules of any given compound are made up alike, it follows that the weight proportions in each molecule must be the same as the weight proportions in the matter as a whole. Each molecule of water must contain 8 parts of oxygen to 1.008 parts of hydrogen, since water in bulk is made up in that way.

But right here a difficulty appears. We need to show *how many* atoms of each kind are contained within a single molecule of water and are thus responsible for these relative weights. If only one atom of each, then the relative **combining weights** are the same as the relative atomic weights. But for all we know in advance, there may be twice as many oxygen atoms as hydrogen atoms, which would make each individual atom of oxygen responsible for only half of the observed relative weight of oxygen.

This difficulty was apparent to Dalton, and he made valiant attempts to surmount it. But another half century of research needed to pass before an Italian chemist, Cannizaro (1858), showed how Avogadro's Principle (§22) might be applied to solve the problem. So many things came into his reasoning that we shall need to postpone it to a later stage of our progress. The half century of research will be worth a chapter in itself.

For the present, then, we shall rest content with knowing that the thing that Dalton vainly tried to do can, after all, be done. The proportions by weight in which elements combine with each other can be made to reveal not only **the relative weights of atoms** but **the relative number of atoms of each kind** in a molecule of any given compound. The table of **International Atomic Weights,** inside the front cover, gives values for atomic weights based on the best recent researches.

38. Chemical Symbols.—Each of the elements is represented by a definite **symbol,** which is the initial letter or pair of letters of its English or Latin name. Thus sulfur is written S; chlorine, Cl; iron (Latin, *ferrum*), Fe; tin (Latin, *stannum*), Sn; mercury (Latin, *hydrargyrum*), Hg. The student should at once commit to memory the symbols of the most common elements—those printed in black type in the list inside the front cover. An alternate exercise, which may be made to serve as a test of one's ability to memorize, consists in committing to memory a list of common metals, with their symbols, in the order of decreasing chemical activity, as given in § 72. We shall later discover some practical advantages in knowing it.

To a chemist, however, the symbol S is much more than an abbreviation for sulfur. It may mean (1) *one atom of sulfur;* or (2) *a weight of sulfur that is proportional to its atomic weight.* The atomic weight of sulfur is 32.064 units; hence S commonly represents 32.064 grams of sulfur. In general, the symbol of an *element represents either an individual atom,* or **as many grams of the element as there are units in its atomic weight.** Such a weight is called a **gram-atom,** or a **gram-atomic-weight.** Thus a gram-atom of oxygen is 16 grams.

How many gram-atoms of carbon in a kilogram of that element?

Which is the greater weight, a gram-atom of silicon, or two gram-atoms of nitrogen?

About what relative numbers of atoms are represented by equal weights of sulfur and oxygen?

39. Chemical Analysis.—Thus far, we have said nothing about the *methods* by which we determine the relative weights of the constituents of a compound. Such a determination, made directly or indirectly, is called a **chemical analysis.** It is a **qualitative analysis** if we merely *identify* the constituents; a **quantitative analysis** if we determine the *amount* of each.

Compounds may sometimes be analyzed **by decomposing them directly,** by means of heat or an electric current. Thus we may weigh crystals of potassium chlorate, then heat them strongly. Oxygen gas will escape, and when all of this has been driven off we may note the loss of weight, and thus determine the percentage of oxygen in the original material. Again, a sample of a copper compound may be dissolved in water, then all the copper plated out in metallic form, on a sheet of platinum, by means of an electric current. The increase in weight of this sheet will then give the weight of copper in the original material.

More commonly, a substance is analyzed indirectly, **by causing it to be transformed into a new substance,** easily weighed, and of known composition.

40. Analysis by Combustion.—A good example of such an indirect quantitative analysis is that used in determining the percentage of each element in such a substance as cane sugar.

A small sample of the sugar is weighed out accurately into a porcelain "boat," which is pushed into a hard-glass tube, contained in an electric furnace (Fig. 14). Most of the tube to the right of the sample is filled with coarse grains of copper oxide, and heated to redness in the beginning, before any heat is applied to the section of the furnace containing the sugar. When all is ready the sample is slowly heated, while a current of dry air or oxygen is passed over it. The sugar is thus slowly decomposed and burned. Any vapors that might otherwise escape oxidation are oxidized at the expense of oxygen yielded up by the layer of red-hot copper oxide over which they are compelled to pass.

The products of the burning are *water vapor,* which is absorbed in a tube containing calcium chloride; and *carbon dioxide,* which passes on through the first tube and is absorbed in a second one, containing soda-lime.* A third tube, containing both soda-lime and calcium chloride, is to protect the others from the moisture and carbon dioxide of the atmosphere.

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* A mixture of quicklime and sodium hydroxide.

The increase in weight of the first tube is multiplied by 11.19 per cent, the percentage of hydrogen in water, to obtain the weight of hydrogen in the original sample; and that of the second tube by 27.28 per cent, the percentage of carbon in carbon dioxide, to obtain the total weight of carbon. If the sum of the weights of hydrogen and carbon is less than the weight of the original sample, at least one other element is present. In the case of sugar this is oxygen.

The preceding description of an **analysis by combustion** should be very carefully studied, since it is the principle by which the composition of practically every member of the vast host of **organic compounds** (§ 321) has been determined.

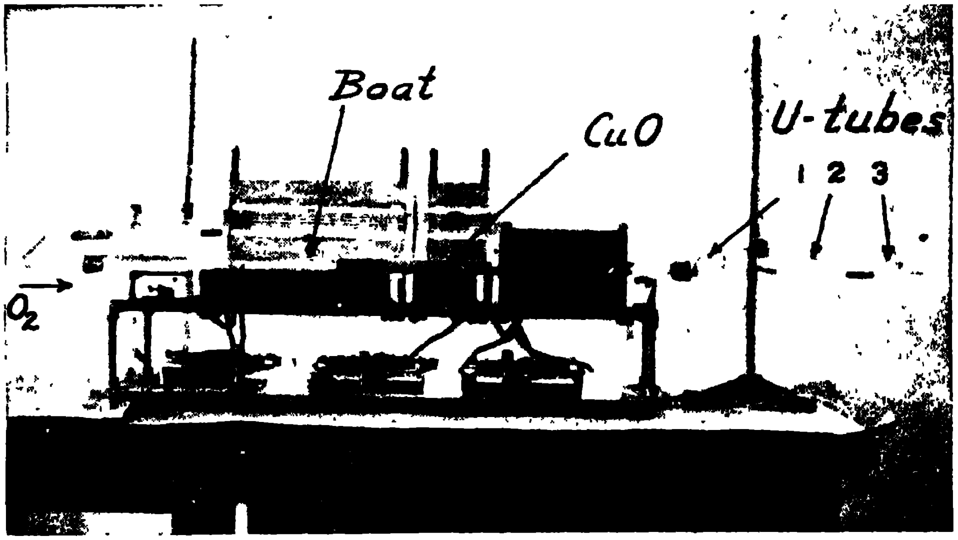

FIG. 14.—Analysis by combustion.

41. Chemical Formulas.— A **chemical formula** is a group of symbols, showing what kinds of *atoms* and how many of each are present in any given *molecule*. **Symbols refer to atoms. Formulas refer to molecules.** Thus an atom of hydrogen is represented by the *symbol* H; but a molecule of hydrogen, which contains two atoms, is represented by the *formula* H_2. The molecules of several common elementary gases can be shown to consist of two atoms, whence the formulas Cl_2, O_2, N_2, etc. But a molecule of helium, argon, or mercury vapor contains but one atom, hence the formulas of these elements are the same as their symbols He, A, Hg.

When we have analyzed a compound, by one of the methods previously described, it is usually easy to calculate the number of atoms of each kind in one molecule of the compound. We shall later (§ 161) show how such calculations are made. As an example, the weight-composition of water, in connection with other evidence, shows that a molecule of *water vapor* consists of two atoms of hydrogen in combination with one atom of oxygen. We therefore represent water vapor by the formula H_2O. There are some reasons for believing that liquid water contains molecules formed by union of two or three of the simple molecules, H_2O, with each other. Moreover, a crystal of ice consists of a vast number of simple molecules interlocked into a unified whole. Still, for simplicity, liquid water and ice are both commonly represented by the simple formula, H_2O, which properly applies only to water vapor. And, in general, **any solid is commonly represented by the simplest formula that agrees with its composition by weight,** though some indefinite multiple of this formula would represent an actual crystal (§ 30).

We sometimes hear chemical formulas spoken of as if they were mere "shorthand signs" for the names of particular substances. In reality, they are much more than this; for each formula shows the kinds of atoms, and the number of each kind that are contained in a molecule of the given substance. And since these atoms have definite average weights, the formula of the compound enables us to calculate the relative weights of the different elements entering into it. Finally, we have formulas, like that in Fig. 2, § 13, which are of the nature of architectural plans, in that they show something about the way in which the atoms are arranged with respect to each other, in space. But more about that later (§ 342).

42. Molecular Weights. Moles.—The average relative weight of the molecules of a given substance, in comparison with a sixteenth part of an atom of oxygen, is called its **molecular weight.** (Note that the unit is the sixteenth part of the oxygen *atom*, the same as in the case of atomic weights.) The molecular weight of any substance is the sum of the relative weights of all the atoms in one molecule of the substance. For water, H_2O, it is therefore . $(2\times1.008)+16=18.016$. Now, just as a chemical symbol may represent a gram atom, so a chemical formula may represent a **gram-molecule,** otherwise called a **mole**—as many grams as there are units in the molecular weight. Thus the formula H_2SO_4 represents two gram-atoms of hydrogen $(2\times$

1.008 g.) in combination with one gram-atom (32.06 g.) of sulfur and four gram-atoms (4×16 g.) of oxygen, forming a total of 98.076 g. of sulfuric acid.

How many grams in a mole of chloroform, $CHCl_3$?

About how many moles of calcium carbonate, $CaCO_3$, are contained in a kilogram of that substance?

Which is the heavier, a mole of nitrogen, N_2, or a gram-atom of sulfur?

A mole of a certain substance is 160 g. What is the relative weight of a molecule of this substance compared with an atom of oxygen?

What is the relative weight of a molecule of the preceding substance compared with a molecule of oxygen?

How many gram-atoms of hydrogen are contained in a mole of hydrogen?

Explain why the word gram-atom applies only to elements, while the word mole applies both to elements and compounds.

Note that a molecule is a small particle, but that a mole is a definite weight of material.

43. Chemical Equations.—If each of the reactants and resultants in a chemical change is represented by its formula, then the change itself may be represented by putting formulas together to make a **chemical equation.** For example, we may write:

$$C + O_2 = CO_2;$$

or,

$$C + O_2 \rightarrow CO_2.$$

Either of these is read: *Carbon* (under proper conditions) *combines with oxygen to form carbon dioxide.* But note the mental reservation: *under proper conditions.* Carbon and oxygen, at ordinary temperatures, do not react; and at higher temperatures, if the supply of oxygen is limited, we get a different product, carbon monoxide. Thus one is not learning chemistry who merely memorizes chemical equations. The most important thing, in the case of each equation, is the **conditions** under which the given reaction takes place; to know, in other words, just how to proceed to obtain the given result in the laboratory.

Metallic copper, when strongly heated in the air, turns black, due to the formation of a film of black copper oxide. If we represent each of these substances by its symbol or formula we have:

$$Cu + O_2 \rightarrow CuO.$$

But this is still incomplete, for O_2 represents a molecule of oxygen, and this contains sufficient oxygen to combine with two atoms of copper, thus forming two molecules of copper oxide (written 2CuO). Thus the completed or **balanced** equation is

$$2Cu + O_2 \rightarrow 2CuO.$$

Notice that a formula represents a single molecule; and therefore when we wish to indicate two molecules of a sustance we simply write a 2 before the formula.

Write an equation to show that when grape sugar ($C_6H_{12}O_6$) is fermented each molecule of the sugar produces two molecules of alcohol (C_2H_5OH) and two molecules of carbon dioxide.

Another to express the fact that when alcohol is burned, each molecule of alcohol requires three molecules of oxygen to react with it, and produces two molecules of carbon dioxide and three molecules of water.

Another to represent the formation of metaphosphoric acid (HPO_3) by combining phosphorus pentoxide (P_2O_5) with water.

Balance the equation just written. Explain what it then means, in terms of molecules.

Read § 49.

44. Some Common Reagents.—A laboratory period may be spent in becoming familiar with some of the common **reagents,** by which we mean materials kept in stock in the laboratory and used to produce chemical reactions. Here are some suggestions, to be amplified by the instructor. Examine the actual substances, until they can be identified when unlabeled samples are passed around the classroom. Incidentally, learn the formulas. Do not try unauthorized experiments.

1. Elements (*a*) *Metals*. Magnesium, aluminium, zinc, iron, tin, copper. Notice the form in which each of these is supplied to your laboratory: whether powder, wire, ribbon, turnings, filings, or granulated metal. Notice which of these metals seem to remain bright in the laboratory atmosphere and which need to be rubbed to expose the metallic surface.

Sodium, potassium. These are very soft metals, which are always kept under kerosene because they react with the moisture of the air. Note the difference in color between freshly cut surfaces of the two metals.

Recall the symbols for all the preceding metals.

(*b*) *Non-metals.*—Solids: Sulfur, charcoal, iodine, red phosphorus, yellow phosphorus. (Do not remove the latter from under water.)

Recall the symbols for all these elements.

Red-brown liquid: Bromine, Br_2. (Do not remove stopper.)
Colorless gases: Nitrogen (N_2); oxygen (O_2); hydrogen (H_2).
Greenish gas: Chlorine (Cl_2). (Do not remove stopper.)

2. Acids.—What is meant by the terms concentrated and dilute (§ 95)? What are some common characteristics of acids (§ 102)?

Concentrated sulfuric acid, H_2SO_4. A heavy, oily liquid (§ 241). Note heat developed when acid is added to water. Danger in adding water to acid, and why?

Concentrated nitric acid, HNO_3. Note the yellowish color (§ 300).

Concentrated hydrochloric acid, HCl. This is a solution of a very soluble, colorless gas, in water (§ 105).

3. Bases.—Sodium hydroxide ($NaOH$) and potassium hydroxide (KOH). These look alike: sticks, flakes, or powder. Sodium hydroxide is common "lye." Best kept in cork-stoppered bottles, since glass stoppers often stick tight. Keep stoppered when not in use. (Expose a small sample in an open dish, to find out why.)

Ammonium hydroxide, **NH_4OH**. Made by dissolving ammonia gas, NH_3, in water (§ 286). This is the "aqua ammonia," or "ammonia water" of the household.

4. Salts.—Most of these are white crystalline solids. Notice how many reagents are sodium, potassium, or ammonium salts. Compare potassium chlorate with common salt (sodium chloride) and with alum to note contrasting crystalline forms.

Copper salts. Green or blue.

Manganese salts. Pink.

Nickel salts. Green.

Iron salts. Some are classed as *ferrous* salts, and some as *ferric* salts. Look for a distinction of color between the two classes.

Potassium permanganate, $KMnO_4$. Purplish-black needles, forming a purple solution.

Potassium dichromate, $K_2Cr_2O_7$. Orange colored crystals. Dissolve a small crystal and observe the color of the solution.

Potassium chromate. Yellow crystals. Dissolve a small crystal, add a few drops of any acid, and draw conclusions.

5. Metallic Oxides.—Note names and colors of three different oxides of lead.

Manganese dioxide, MnO_2. Dark brown powder.

45. Standard Manipulation. Chemistry is a manipulative science. The things we know about the transformations of matter were not derived by pure meditation nor revealed to the chemical pioneers in dreams. Every chemical equation is based on prolonged experiments (§ 164); and each triumph of the human intellect, in the realm of atoms and molecules, had to wait for the effort of human hands.

Actually, a large part of the difficulty of those who have difficulty with chemistry may be traced to a bookish habit of mind which leads them to pay more attention to formulas on a printed page than they do to what they see on the lecture table or perform with their own hands. They rest content with learning text-book facts about things never distinctly visualized at all. They fail to become vividly conscious of the actual experimental conditions under which substances are made to interact and of the means that are used to separate substances from each other.

The remedy is to be found in laboratory exercises, taught in such a way as to enforce consideration of the substances themselves rather than mere *names of substances*. One who has not learned how to do things with chemistry has studied the science in vain. Standard pieces of apparatus may be exhibited in the laboratory, and standard manipulation illustrated on the lecture table; and students from the beginning should be taught to sketch apparatus from memory, at least with half the skill with which the Cave Men used to sketch reindeer. Lecture experiments, not too numerous, should lay stress on what is being done, and how, and what the results are intended to prove. These should be covered in the quiz.

Study the following:

1. Heating a Solid to Produce a Gas. (Fig. 15.)—Note the proper inclination of the test-tube *A*, and why. If the gas is only very slightly soluble it is collected in small bottles, previously filled with water and inverted over the end of the delivery tube, where they are supported by a *bridge*, *B*, just beneath the surface of water in a *pneumatic trough*, *T*. How may one determine whether the apparatus is gas tight?

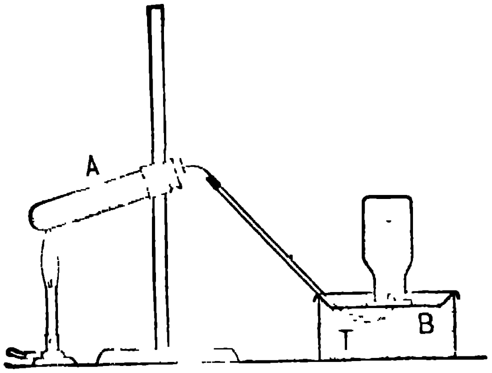

FIG. 15.

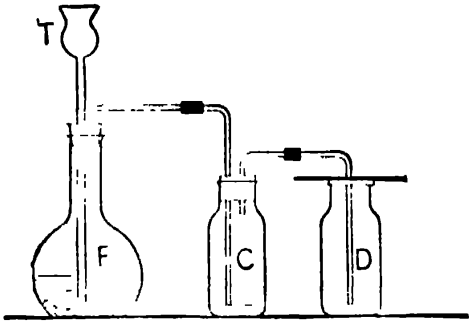

FIG. 16.

2. Reaction between a Liquid and a Solid to Produce a Gas. (Fig. 16.)—The liquid is added through a *thistle-tube*, *T*. Note that this must be inserted far enough to dip beneath the surface of the liquid in the flask. Why? Sometimes a *wash-bottle*, *C*, containing a very little water, is used to wash the escaping gas, to remove impurities. An empty wash-bottle often serves to catch spray from the liquid in the generator, *F*. If the washed gas happens to be soluble in water, and thus incapable of being collected over water, it is collected in a bottle, *D* (covered with cardboard or glass). The sketch assumes that the gas is heavier than air. Show how the apparatus would be modified in the contrary case.

Study the Kipp generator (Fig. 26). What advantage does it have over the apparatus shown in Fig. 16?

3. Reaction of a Gas with a Solid. (Fig. 17.)—The solid is usually contained in a *porcelain "boat," B*, about two inches long. This is placed inside a hard-glass tube, *H*, which is gradually heated to a dull redness with the Bunsen burner, while a current of the gas is being passed.

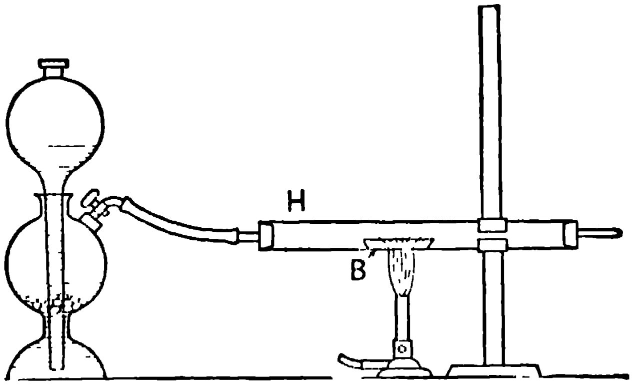

Fig.

EXERCISES

Use Approximate Equivalents

1. How many liters in a cubic meter?

2. How many square centimeters in a square inch?

3. A pressure of 1033 g. per square centimeter is how many pounds per square inch?

4. If 1 cc. of air weighs 1.29 mg., how many liters in 1 kg. of air?

5. What weight of sugar is contained in one liter of a sugar solution, which is 1.4 times as heavy as water, and contains 30 per cent sugar by weight?

6. What is the height, in meters, of a column of water which exerts a pressure of 1 kg. per square centimeter?

7. If a liter of air weighs 1.29 g., calculate the volume, in cubic meters, of 1000 kg. of air. Express the result as a power of ten, as explained in a footnote, p. 35.

8. What linear distance, in centimeters, corresponds to a volume of 1 cc. when a liquid is contained in a capillary tube of 0.2 sq. mm. cross-section?

9. In a certain reaction, 50 parts by weight of substance *A* react with 35 parts by weight of substance *B* to produce 45 parts by weight of *C* and an unstated weight of *D*. What will be the weight of *D*? State the law that applies.

10. Make a statement about the rusting of iron in moist air that will illustrate the Law of Conservation of Weight.

11. Lead combines with oxygen in several different proportions to form a corresponding number of different oxides of lead. Is this an exception to the Law of Constant Composition? Why or why not?

12. Explain why the Law of Constant Composition is only a special case of the Law of Definite Proportions.

13. State Dalton's Principle, and show how it applies to water.

14. Make a general statement regarding the atomic weight of samples of a given element from different geographical sources.

15. What is the unit weight in tables of atomic weights?

16. Explain why determinations of atomic weights are of practical interest.

17. Are all the atoms of a given element necessarily of the same weight? Make a definition of atomic weight consistent with this fact.

18. What sort of experimental data have been used in deducing our modern tables of atomic weights?

19. One of the oxides of lead contains 103.5 parts of lead in combination with 16 parts of oxygen. This fact alone is not sufficient to establish the atomic weight of lead. Explain why.

20. Explain the difference between the symbol of an element and its formula. Tell why the two are sometimes identical and sometimes not.

21. What weight of each element is contained in one mole of chloroform, $CHCl_3$? What percentage of the total weight is chlorine?

22. Explain why the word symbol applies only to elements, and the word formula both to elements and compounds.

23. What is the symbol of chlorine? What is its formula? What actual weight of chlorine is represented by each?

24. What facts about sulfuric acid are expressed by its formula, H_2SO_4?

25. What weight of sulfur is combined with 64 g. of oxygen, in sulfuric acid?

26. What fraction of a mole of sulfuric acid is needed to contain 8 g. of oxygen?

27. What total weight of sulfuric acid is represented by one mole of that substance? What percentage of that weight is sulfur?

28. Similarly, determine the percentage of copper in copper oxide, CuO.

29. Similarly, determine the percentage of each element in potassium dichromate. (Use nearest whole numbers for atomic weights.)

30. From your experience with the preceding problems, give a general rule for determining the percentage of each element in a compound whose formula is known.

31. When calcium carbonate, $CaCO_3$, is treated with hydrochloric acid, the reaction produces calcium chloride, $CaCl_2$, together with carbon dioxide and water. Write and balance an equation to illustrate.

32. In the preceding equation, how many moles of hydrochloric acid, and what actual weight of hydrochloric acid, is needed to react with one mole of calcium carbonate?

33. How many moles of calcium carbonate are represented by 100 g. of that substance. How many moles of calcium chloride, and what weight of calcium chloride will that produce.

34. From the preceding result, calculate the number of grams of calcium chloride which can be produced from 10 g. of calcium carbonate.

35. Distinguish between the following: Reactant, resultant; molecule, mole; symbol, formula; atomic weight, gram-atom; qualitative analysis, quantitative analysis; reagent, reactant; atomic weight of an element, actual weight (in grams) of one atom of an element.

36. Look up a few biographical details concerning Dalton and Cannizzaro.

37. Explain how the molecular weight of a substance may be calculated, if we know its formula.

38. Is the unit of molecular weight the same or different from the unit of atomic weight? What is the atomic weight of oxygen? Its molecular weight?

39. Sulfur dioxide gas (volume for volume) is twice as heavy as oxygen. What may we conclude about the molecular weight of sulfur dioxide? State the principle involved.

40. Knowing the molecular weight of oxygen to be 32, state what experimental information needs to be determined concerning any other gas (§ 22), in order that its molecular weight may be calculated.

CHAPTER IV

OXYGEN

46. Oxygen the Most Abundant Element.—Oxygen makes up fully half of the earth's crust, including the solid rocks, soil, ocean, and atmosphere (§ 12). Most of this is in *chemical combination* with other elements—atoms of oxygen united in a definite ratio with atoms of other elements to form molecules of chemical compounds (§ 13). Examples are quartz, limestone, clay, and other common minerals. **Water is very closely eight-ninths oxygen and one-ninth hydrogen, by weight.** Finally, all living plants and animals contain oxygen, in chemically combined form.

But in the atmosphere oxygen is for the most part *uncombined.* Air is indeed not a chemical compound, but a *mixture,* formed by intermingling molecules of oxygen with those of nitrogen and other gases. Its chemical composition (§ 7) therefore varies slightly from place to place and from time to time. But on the average, **air is roughly one-fifth oxygen and four-fifths nitrogen.***

47. The Discovery of Oxygen.—The Chinese, as early as the eighth century, apparently observed that air contains at least two components, one of which is able to support combustion, while the other is not. The Moorish alchemist, Geber, who lived in Seville about the year 800, discovered that many metals grow heavier when heated in open vessels, for the reason, as we now know, that they unite with the oxygen of the air.

Here progress halted for almost a thousand years, until Scheele, in Sweden (1771), prepared oxygen by heating several solid substances and showed that it is probably present in the air; Priestley, in England (1774), prepared it from mercuric oxide; and Lavoisier, in France (1777), confirmed the previous observations, and showed the part that oxygen plays in respiration and combustion.

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* More exactly about 21 per cent oxygen by volume, or 23 per cent by weight, with about 1 per cent of argon, and the rest nearly all nitrogen.

One of the experiments of Lavoisier is justly famous as proving clearly that air is not an element—as the world long believed on the authority of Aristotle—but contains at least two distinct substances.

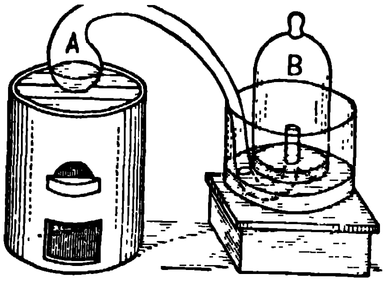

FIG. 18.

Mercury was heated in a retort (*A*, Fig. 18) the neck of which led under a bell-jar (*B*) standing in a larger dish of mercury. A red powder soon appeared in the retort, and slowly increased in quantity during twelve days. The air enclosed with the mercury decreased at the same time, presumably because a part of it was combining with the mercury, to produce the red powder.

But after twelve days' heating no further change seemed to take place. The red powder was then collected and heated still hotter. This decomposed it, giving back metallic mercury and a gas. The latter, moreover, proved to have exactly the same volume as the air that disappeared in the first part of the experiment.

It was accordingly concluded that air consists of at least two ingredients. The one, making up about a fifth of the whole, and able to unite directly with mercury to form the red powder (mercuric oxide), Lavoisier named *oxygen*. The rest, which failed to combine with mercury even after long-continued heating, has since been shown to consist largely of nitrogen (§ 280).

48. Oxygen from Potassium Chlorate.—Though oxygen is such a plentiful element, it is often so firmly united with other substances as to be separated with great difficulty. Ordinary white sand, for example, is more than half oxygen, yet fails to release this element, even when heated to the temperature of the electric arc (3500° C.). Water (or steam) is eight-ninths oxygen, and is decomposed only very incompletely under the same conditions.

But among the many substances rich in oxygen are a few which do give it off when they are heated to a moderately high temperature. The one most commonly used in the laboratory is a white crystalline substance, potassium chlorate. This may be melted in a test-tube, by gentle heating, without being decomposed appreciably; but when a small amount of manganese dioxide is added, oxygen gas is given off very rapidly, and may be recognized at the mouth of the test-tube by the common **test for oxygen**—the fact that it will cause a glowing spark, at the end of a splinter of wood, to burst into flame.

Or the potassium chlorate and manganese dioxide may be mixed in the beginning, and heated in an inclined test-tube, the oxygen gas being collected over water in a pneumatic trough.

(Study Fig. 15, p. 51.) In the absence of the manganese dioxide, the action takes place more slowly, and a higher temperature is required, but the same products are obtained in the end. The **potassium chlorate** ($KClO_3$) parts with all of its oxygen, leaving behind another white solid, **potassium chloride** (KCl), mixed with the black manganese dioxide, which remains undecomposed.

49. How Equations are Recalled.—Read § 43. The preceding experiment may be summarized as follows:

$$\text{potassium chlorate} \rightarrow \text{potassium chloride} + \text{oxygen}.$$

But potassium chlorate is known to have the formula $KClO_3$, and potassium chloride the formula KCl; while uncombined oxygen is O_2 (§ 41). Substituting formulas for the names first written:

$$KClO_3 \rightarrow KCl + O_2.$$

This formulation is **unbalanced;** for there are three atoms of oxygen in each molecule of potassium chlorate, and only two of these are accounted for among the products. We adjust this by taking two molecules of potassium chlorate, $2KClO_3$, which will give us two molecules of potassium chloride, $2KCl$, and three of oxygen, $3O_2$; i.e., six atoms of oxygen, two of potassium, and two of chlorine on each side of the equality sign. The balanced equation accordingly stands:

$$2KClO_3 = 2KCl + 3O_2.$$

An equality sign has here been substituted for the arrow, to direct attention to the fact that the process of balancing has been completed.

Notice that the process of recalling an equation is carried out in three steps.

(1) Recall the names of the substances entering into the chemical change, and the names of those produced by it.

(2) Translate these names, one by one, into formulas.

(3) Balance the equation by taking such multiples of the indicated formulas as will result in equal numbers of atoms, for each given element, to the right and left of the equality sign. *For details of this process, the student should now study* § 128.

Of these three steps, the first is the most important. Skill in balancing will come with practice.

50. An Important Warning.—Potassium chlorate, $KClO_3$, gives off *all* of its oxygen when heated. Potassium nitrate, KNO_3, gives off only *a third* of its oxygen, even at very high temperatures, and leaves behind potassium nitrite, KNO_2. Calcium carbonate, $CaCO_3$, gives off *no oxygen at all*, but carbon dioxide. Potassium metaphosphate, KPO_3, is *unaffected by heat*. The equations are:

$$2KClO_3 = 2KCl + 3O_2;$$
$$2KNO_3 = 2KNO_2 + O_2;$$
$$CaCO_3 = CaO + CO_2;$$
$$KPO_3 = KPO_3.$$

These examples show very plainly that **a formula affords no safe clue to what will happen when a substance is heated or when it reacts with other substances.** $KClO_3$, KNO_3, $CaCO_3$, KPO_3 all behave differently when heated, in spite of their similar formulas.

Do not make chemistry into a species of algebra. In algebra we know that if $(a+b)^2$ is written on the left-hand side of the equation, then $a^2+2ab+b^2$ may be written on the right-hand side. In chemistry, from the formulas of two or more substances, there is absolutely no way of predicting what the formulas of the products of their interaction will be. An experienced chemist reasons, not from formulas at all, but from his knowledge of the general *properties* of the given substances or of their close relatives. The intelligent student soon learns enough chemistry to enable him to begin to reason from properties, as a trained chemist might do. Until then, there is no way to " figure out " what will happen when two substances are brought together. *One simply must know.* Students who heed this warning should make comfortable progress in chemistry. Those who do not are headed toward failure from the very first week.

51. Oxygen from Sodium Peroxide.—When metallic sodium is heated in a slow current of air (§ 434) it forms a yellow powder, sodium peroxide (Na_2O_2). When this is added to cold water, the mixture gives off oxygen gas, very slowly at room temperatures, more rapidly in the presence of a little copper oxide, or on being warmed. (It is very dangerous to add sodium peroxide to *hot* water, for the reaction then takes place with explosive violence.)

The final products are sodium hydroxide (NaOH) and oxygen;

$$Na_2O_2+H_2O \rightarrow NaOH+O_2.$$

This equation is harder to balance than most of those to be met in the next few chapters. Balanced, it reads:

$$2Na_2O_2+2H_2O=4NaOH+O_2.$$

How many *molecules* of each of the four substances are here indicated? How many *atoms* of oxygen (combined and elementary) on each side of the equation? How many moles (§ 42) of sodium hydroxide may be formed from two moles of sodium peroxide? How many moles of oxygen will be liberated at the same time? What weight of oxygen will this be?

52. Catalyzers and Catalysis. Enzymes.—A very small amount of manganese dioxide (or ferric oxide) will cause potassium chlorate to be decomposed more rapidly, or at a lower temperature, than would otherwise be possible. Copper oxide is of similar service in furthering the decomposition of sodium peroxide by water. Many other cases are known in which substances change the speed at which reactions take place, without being themselves permanently altered. These substances are called **catalyzers,** or **catalytic agents.*** The phenomenon of increased speed of reaction, in the presence of catalyzers, is called **catalysis,** or **catalytic action.** Some instances are known in which one part of a catalyzer is sufficient to transform as much as one hundred million parts of other material.

The mode of action of catalyzers has been carefully studied, and in some cases has been sufficiently well explained; but we are still ignorant of the manner in which many others produce their effects. All we know is that they aid a process that otherwise would take place with difficulty. They are a little like oil on a rusty bearing.

Catalyzers play a very important part in nature and industry. The "drying" of linseed oil, for example, is really a process union with oxygen, not one of evaporation at all. It is very much hastened by using oil that has been "boiled" with lead oxide, which acts as a catalyzer. Many important chemical substances, such as sulfuric acid, nitric acid, and ammonia, are now manufactured on a large scale with the aid of catalyzers. All living cells contain natural catalyzers, called *enzymes* or *ferments*, which make possible the chemical changes carried out in vital processes.

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* In what follows, the word catalyzer will refer to positive catalyzers, or those that increase the speed of a reaction; though negative catalyzers, which decrease reaction speed, are also known.

53. Oxygen from the Oxides of the Noble Metals.—Certain metals, such as silver, mercury, gold, and platinum (often referred to as **noble metals**) are more difficult to bring into combination with oxygen than such other familiar metals as iron, zinc, and lead; and their oxides, once formed, are easily decomposed by heat, liberating oxygen.

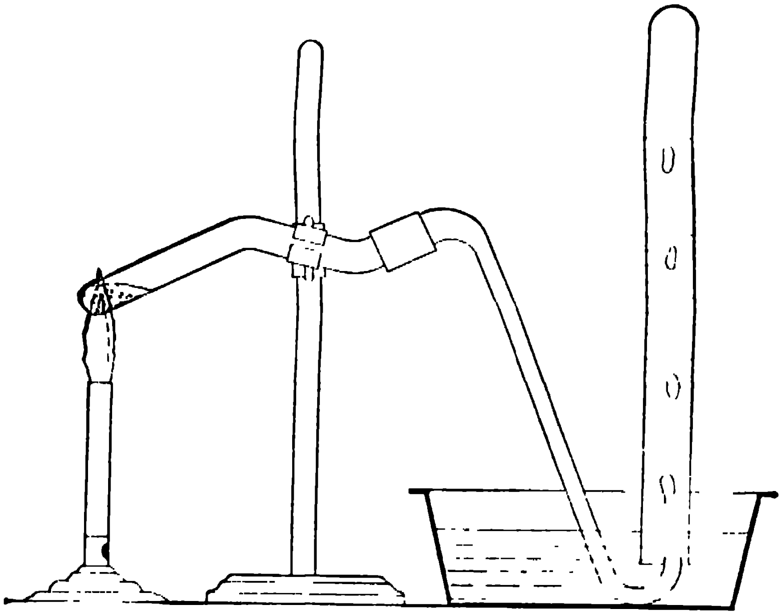

FIG. 19.—Preparing oxygen from mercuric oxide.

This property of mercuric oxide was used by Lavoisier in his famous research on the composition of the atmosphere (§ 17).

$$\underset{\text{Mercuric oxide}}{2HgO} = \underset{\text{Mercury}}{2Hg} + O_2.$$

Fig. 19 shows the experiment as performed in the lecture room. The mercury produced is driven off as a vapor, which condenses in the turn of the tube. The gas produced in the process may be recognized as oxygen by the fact that a glowing splinter of wood, held at the mouth of the test-tube, bursts into flame.

54. Commercial Oxygen.—Water may be decomposed by an electric current, into hydrogen and oxygen (§ 65). This is one of the methods by which oxygen is produced commercially, for oxy-hydrogen and oxy-acetylene welding (§ 59).

A cheaper source of commercial oxygen is **liquid air.**

Every one who has inflated tires with a hand-pump knows that air is heated when compressed. This is because mechanical energy, expended in moving the piston of the pump, is converted into heat energy. Conversely, when a gas expands, driving a piston outward against the pressure of the atmosphere, heat energy is converted into mechanical energy, and the gas is cooled. This principle is applied in the Claude process for the manufacture of liquid air, outlined in Fig. 20.

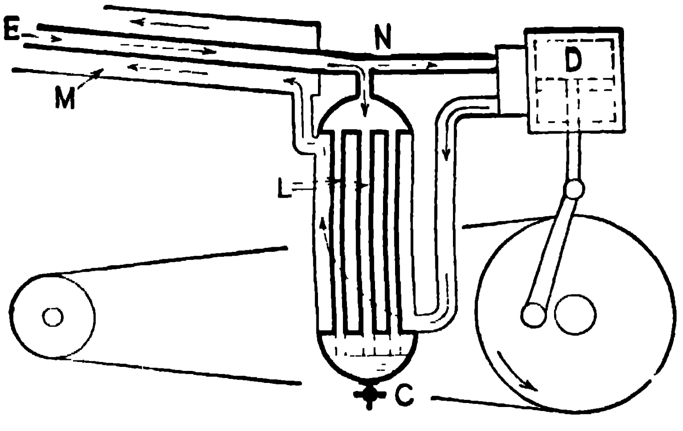

Fig. 20.—Principle of the Claude liquid air machine.

Air is carefully freed from dust, moisture, and carbon dioxide, then compressed by powerful pumps. The heat liberated is removed by passing the compressed air through a cooling coil, surrounded by running water. Thus purified, compressed, and cooled, it passes through the inner tube *E* of a long metallic coil, into an engine cylinder, *D*, in which it expands—pressure falling from 40 atmospheres to 1 atmosphere. The mechanical energy produced in this way may be made to help compress new portions of air.

The expanded air, now very much colder, passes around the outside of a set of tubes in the liquefier, *L*, then out through the pipe, *M*, which surrounds the current of incoming air, in *E*. This is cooled, and in expanding in the engine cylinder is cooled still further. Thus the temperature of the incoming air falls lower and lower. Finally a part of it, passing through the branch, *N*, into the interior of the tubes in *L*, is condensed to liquid, and collects in *C*. Its temperature is about −140° C.

Liquid air thus produced is approximately four-fifths nitrogen and one-fifth oxygen. But if it is permitted to evaporate, the nitrogen, being the more volatile, passes off first, leaving almost pure liquid oxygen behind. The process described above may be so modified that the part of the air condensed is largely oxygen; while that passing on is nearly pure nitrogen, which has a number of important commercial uses of its own (§ 282).

55. Oxidation and Reduction.—Any process in which oxygen is made to combine with a given substance is called **oxidation.**

The substance that gains oxygen is said to be **oxidized.** We have seen that mercury is oxidized when heated for a long time in air (§ 47). The rusting of iron is oxidation. So is the burning of a combustible substance in the air, the turning of hard cider into vinegar, respiration (§ 325), the drying of paints (§ 52), certain modern methods for the disposal of sewage, and processes of decay in general—for in all of these the oxygen of the air is made to combine with other things.

The converse process, in which a substance parts with oxygen, is called **reduction.*** The substance thus deprived of oxygen is said to be **reduced.**

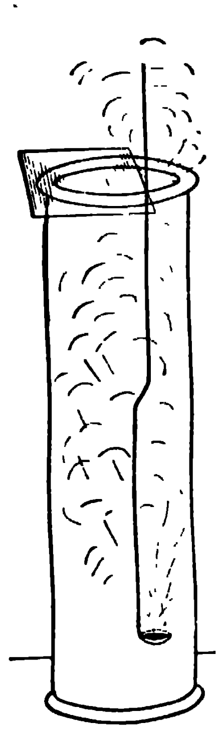
Fig. 21.—Burning sulfur in oxygen.

56. Combustion in Air or Pure Oxygen.—Rapid oxidation, accompanied by light, and resulting in a high temperature, is called **burning,** or **combustion.** Before a substance will burn it must be heated to a certain **kindling temperature.** The effect of friction on a match-head, or a flame at the tip of a cigar, or a spark in a mixture of air and gasoline vapor in the cylinder of an automobile engine, is to heat the combustible material up to the kindling temperature. Oxidation often takes place slowly even at room temperature. But it becomes more and more rapid as the temperature is raised, and at the kindling temperature heat is liberated fast enough to counterbalance that lost by radiation and conduction. The temperature is thus maintained at the kindling temperature, and the combustion continues so long as both air and fuel hold out.

Many elements, such as sulfur (Fig. 21) and carbon, that burn rather feebly in ordinary air, blaze up brilliantly and burn very rapidly in pure oxygen. Finely powdered iron will burn in air if thrown into the flame of a gas burner. But iron rods of considerable size can be made to burn in oxygen.

It is a very fortunate circumstance that the oxygen of the air is diluted with so much nitrogen. For in an atmosphere of pure oxygen the grates of a furnace would not last long. Smokers would find little comfort in such a situation, for an ordinary cigar would flare up and disappear in a few seconds. One may even doubt whether we could long exist with vital processes so much quickened as they would be in pure oxygen. As Priestley once expressed it: "We would live out too fast."

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* The words oxidation and reduction have other, much broader meanings, stated hereafter.

57. Oxides.—The product formed when oxygen unites with another element is called an **oxide.** Sometimes oxides are *gases*:

$$S+O_2=\underset{\text{Sulfur dioxide}}{SO_2};$$

$$C+O_2=\underset{\text{Carbon dioxide}}{CO_2}.$$

Other oxides are solids:

$$2Mg+O_2=\underset{\text{Magnesium oxide}}{2MgO};$$

$$2Na+O_2=\underset{\text{Sodium peroxide*}}{Na_2O_2};$$

$$4P+5O_2=\underset{\text{Phosphorus pentoxide}}{2P_2O_5};$$

$$3Fe+2O_2=\underset{\text{Magnetic iron oxide†}}{Fe_3O_4}.$$

Here again we may note that it is impossible to predict, by any process of algebra, what the formula of the product of a reaction will be. At first it is most important for the student to remember the *names* of substances produced in chemical reactions, and *what they look like.* Skill in writing equations will come with practice.

58. Metals and Non-metals.—1. If a very small amount of water is added to a bottle in which magnesium or sodium has been burned in oxygen, the oxide will unite with the water to form a solution that will turn red litmus *blue.*

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* The name peroxide signifies, among other things, that the given element is here combined with the greatest possible amount of oxygen.

† So called to distinguish it from other oxides of iron.

$$MgO+H_2O=\underset{\substack{\text{Magnesium}\\ \text{hydroxide}}}{Mg(OH)_2};$$

$$2Na_2O_2+2H_2O=\underset{\substack{\text{Sodium}\\ \text{hydroxide}}}{4NaOH}+O_2.$$

Such a solution is said to have a **basic** or **alkaline** reaction. The metallic hydroxide that is formed is called a **base.** The element that was burned is then said to be a **base-forming element,** or an **electro-positive element,** or a **metal.** These three terms mean the same thing.

2. But if a small amount of water is added to a bottle in which sulfur, carbon, or phosphorus has been burned, the oxide of that element will unite with the water to form a solution that will turn blue litmus *red.*

$$SO_2+H_2O=\underset{\substack{\text{Sulfurous}\\ \text{acid}}}{H_2SO_3};$$

$$CO_2+H_2O=\underset{\substack{\text{Carbonic}\\ \text{acid}}}{H_2CO_3};$$

$$P_2O_5H_2O=\underset{\substack{\text{Metaphosphoric}\\ \text{acid (§313)}}}{2HPO_3}.$$

Such a solution is said to have an **acid** reaction. The substance that is formed is called an **acid.** The element burned is said to be an **acid-forming element** or an **electro-negative element,** or a **non-metal.** *These three terms mean the same thing.*

To summarize: **If the oxide of an element dissolves in water to form a solution turning red litmus blue (alkaline reaction) the element concerned is a metal; if the oxide dissolves to form a solution turning blue litmus red (acid reaction) the element is a non-metal.**

But it must be emphasized that **it is not always possible to determine whether an element is a metal or non-metal by this test.** For its oxide may be insoluble in water, or may give a solution too feebly alkaline or acid to affect litmus. Moreover, a number of the elements are variable in character. Aluminum, for example, is a veritable Jekyll and Hyde, behaving now as a metal and now as a non-metal.

59. Uses of Oxygen. – 1. Oxygen is used in medicine for the relief of impeded respiration (e.g., pneumonia), and in the treatment of cases of poisoning by nitric acid fumes, somewhat frequent among workmen engaged in manufacturing explosives.

2. In producing anæsthesia with nitrous oxide (§ 293), oxygen is usually administered as well.

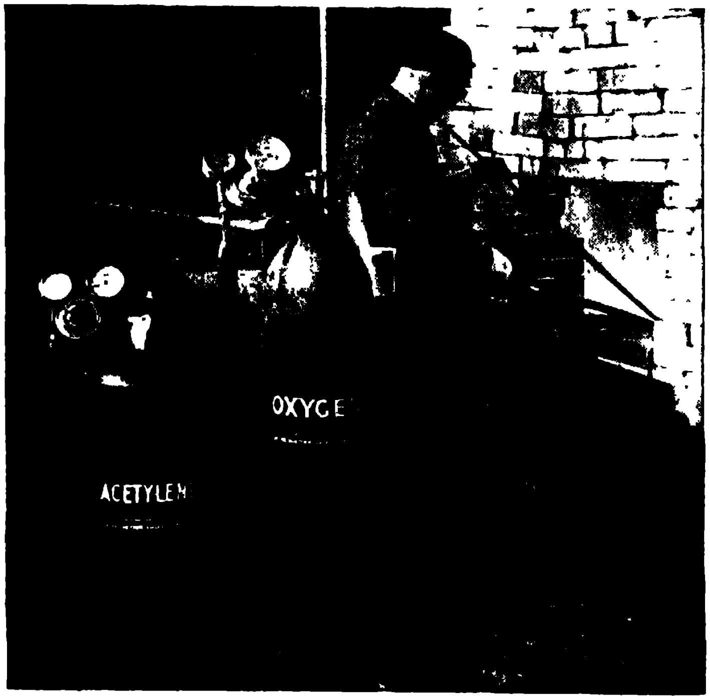


Fig. 22.—Welding a cracked locomotive cylinder with oxy-acetylene blowpipe. The two gases, led through separate tubes, mingle near the tip of the burner.

3. Another application is in the **oxy-acetylene** or **oxy-hydrogen blowpipe** (*Fig. 22*) invented by *Robert Hare, one of America's* chemical pioneers.

This instrument gives a much higher temperature than would be reached by either acetylene or hydrogen burning in air, for the nitrogen of the air dilutes and cools the flame-gases. The oxy-hydrogen blowpipe is of importance in melting platinum and in the manufacture of fused silica ware and artificial rubies— though for such purposes it has been in part replaced by special forms of the electric furnace. It remains of considerable service, however, in tearing down the steel frameworks of obsolete or damaged buildings, in cutting manholes in steel plates, and for similar purposes. It has recently been so improved that it will burn under water, and is used in salvaging sunken vessels.

The applications of oxygen are important and are increasing day by day, in spite of its present high price—over $200 a ton. Some one has estimated that the industries consume at least 20,000,000 cubic meters or 30,000 tons of oxygen gas each year. But recent improvements in the commercial methods for the liquefaction of air (§ 54) should shortly enable oxygen and nitrogen to be produced much more cheaply. We may then see oxygen transported in pipes, like water or illuminating gas, instead of in clumsy steel cylinders. Revolutionary changes may thus be produced in many industries requiring high temperatures: the manufacture of glass and fused silica; the reduction of iron and aluminum from their ores; the manufacture of sulfuric acid and calcium carbide. Perhaps coal gas may again win favor as a source of illumination—for the efficiency of the common gas mantle (§ 593) would be increased many fold if it were heated to a higher temperature than that now reached. But these are all problems of the future.

60. Ozone.—Ozone is a *form of oxygen* distinguished by its **extraordinary chemical activity.** Thus, metallic silver, which remains bright for years in ordinary oxygen, becomes covered with a brown film of an oxide of silver when exposed to air containing a trace of ozone.

The peculiar pungent odor of ozone is often noticed in thunder storms, and around wireless transmission sets or other high-tension electrical apparatus. It is formed in nature whenever a lightning discharge passes through the air, and is constantly produced in the upper regions of the atmosphere by the action of the ultraviolet light of the sun's rays on ordinary oxygen. But ozone as such never lingers very long in the air, for it reacts with the water vapor which is always present, to form hydrogen peroxide, H_2O_2.

In the laboratory, dry air may most easily be ozonized by passing it between two plates charged at a potential of several thousand volts from a source of alternating current. The silent electrical discharge that takes place between the plates is usually accompanied by a pale bluish light, rich in ultraviolet rays, and the air leaving the apparatus is found to contain a per cent or so of ozone.

When ozone oxidizes other substances, only a third of its oxygen is yielded up. This is taken to mean that a molecule of ozone contains three atoms, instead of the two characteristic of the ordinary form of oxygen—and that one of these three is able to part company with the other two, and attach itself to something else. Ozone is therefore represented by the formula O_3; and its formation from ordinary oxygen is given by the equation:

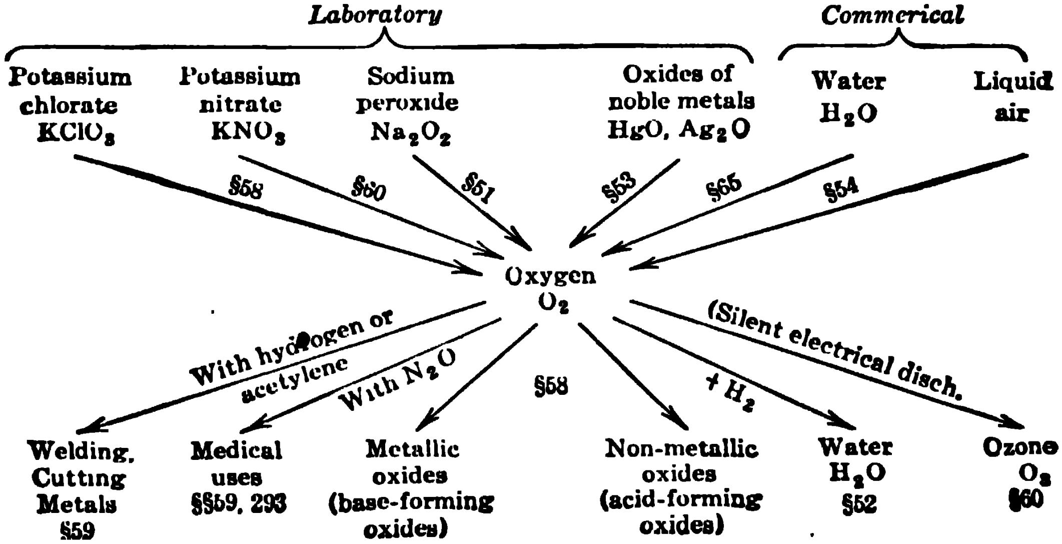
$$\underset{\text{Oxygen}}{3O_2} \rightarrow \underset{\text{Ozone}}{2O_3}.$$

When the third atom of ozone, responsible for its activity as an oxidizing agent, has taken its departure, the other two appear as a molecule of ordinary oxygen.

Small amounts of ozone in the atmosphere are best detected by the fact that it produces a deep blue color in paper that has been dipped in a solution containing *starch* and *potassium iodide.* But this test is not an entirely conclusive one, for chlorine and a few other substances produce the same result. Ozone may be liquefied at very low temperatures to a deep blue liquid, which sometimes decomposes explosively.

Ozonized air is sometimes used for **sterilizing drinking water,** and has the advantage over other chemical substances of leaving behind no product other than oxygen after it has done its work.

61. Graphical Summary.


Laboratory
Commerical
Potassium chlorate $KClO_3$
Potassium nitrate KNO_3
Sodium peroxide Na_2O_2
Oxides of noble metals HgO, Ag_2O
Water H_2O
Liquid air
§58
§60
§61
§53
§65
§54
Oxygen O_2
With hydrogen or acetylene
With N_2O
§58
$+H_2$
(Silent electrical disch.
Welding, Cutting Metals §59
Medical uses §§59, 293
Metallic oxides (base-forming oxides)
Non-metallic oxides (acid-forming oxides)
Water H_2O §52
Ozone O_3 §60

Sources of oxygen.

EXERCISES

1. Four jars contain, respectively, oxygen, air, carbon dioxide, and sulfur dioxide. Tell how you would identify each.

2. If a liter of oxygen weighs 1.429 g., how many liters can be prepared from 1 kg. of potassium chlorate (which contains 36.19 per cent oxygen)?

3. If a liter of oxygen weighs 1.429 g., how many liters can be prepared by decomposing 100 cc. of water (§ 16) with an electric current?

4. What are the chief present uses of oxygen? Some possible future uses?

5. What is meant by *alkaline reaction*, *electro-negative element*, *enzyme*, the *chemical composition* of a substance?

6. What is the distinction between a *material* and a *substance*? Which is potassium chlorate? Air?

7. A white powder is known to be either magnesium oxide or phosphorus pentoxide. What is a simple way to determine which it is? What fact does this test indicate concerning the elements magnesium and phosphorus? State the principle involved.

8. Look up some biographical details concerning Scheele, Priestley, and Lavoisier.

9. What is meant by the statement, "Light catalyzes the decomposition of hydrogen peroxide"? Write an equation to represent this change, assuming the products to be oxygen and water.

10. Write and balance an equation to express the change that takes place when metallic sodium is heated in the air (§ 51).

11. What weight of sodium peroxide can be made from 16 g. of sodium?

12. Write and balance an equation for the action of ozone on water.

CHAPTER V

HYDROGEN

62. Occurrence.—Elementary hydrogen (i.e., hydrogen present as an *element,* in a *free,* or *uncombined* condition) is found in the gases escaping from petroleum and natural gas wells and certain volcanoes. Coal-gas (§ 350) and especially "water-gas" (produced by action of steam on coal or coke, § 69) contains noteworthy amounts of hydrogen. Small amounts are often formed in fermentation and decay.

Only traces of hydrogen occur in the lower levels of the earth's atmosphere, though it appears to be an important constituent of the highly rarefied air that is found at heights of twenty miles or more. Enormous quantities are found in the atmosphere of the sun; and during solar eclipses vast whirlpools of incandescent hydrogen may be observed, darting out from the solar rim for thousands of miles.

Hydrogen, in combination with other elements, is very abundant, though not nearly so much so as oxygen (§ 12). **Water is one-ninth hydrogen.** Combined with carbon, hydrogen is found in gasoline, lubricating oil, and other petroleum products. Combined with carbon and oxygen, it is contained in wood, paper, starch, and fats. Combined with carbon, oxygen, nitrogen and other elements, it forms a large part of almost all the constituents of our foods and the tissues of living plants and animals. **All acids** contain hydrogen, as do ammonia, alcohol, formaldehyde, perfumes and dyes, and many other products of chemical industry.

63. Discovery of Hydrogen.—That an inflammable gas is produced when dilute acids act upon certain metals was known to the alchemists, the predecessors of our modern chemists, at least four hundred years ago. But the first person to separate hydrogen from other gases and recognize it as a separate substance was the English physicist, Cavendish, in 1766. He obtained it not only from acids, but by the action of steam on red-hot iron (§ 66).

These experiments were repeated independently by Lavoisier, who named the new gas hydrogen (Greek, *water-former*), in recognition of the fact that water is formed when it combines with oxygen.

64. Sources of Hydrogen.—Hydrogen is commonly prepared by the following methods:

1. **From water.** This is decomposed

(*a*) By an electric current.

(*b*) By certain metals, with or without the aid of heat.

(*c*) By carbon at high temperatures.

(*d*) By certain metals, and silicon, in the presence of solutions containing sodium hydroxide.

2. **From non-oxidizing acids,** such as dilute hydrochloric and sulfuric acids, which react with certain metals.

3. Mixed with large quantities of other gases, by the decomposition of wood, coal, and petroleum at high temperatures, in the absence of air.

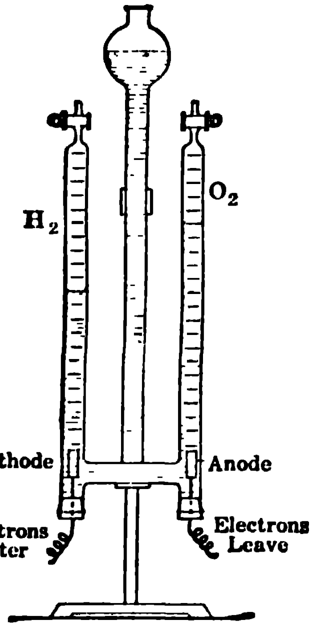


FIG. 23.—Electrolysis of water.

65. Electrolysis of Water.—Whenever an electric current is passed through a solution, chemical changes occur, both at the place where the current enters and at the place where it leaves. The process is called **electrolysis.** The liquid which conducts the current, and in which the chemical change takes place, is called the **electrolyte.** If this is a solution, it is sometimes the dissolved substance and sometimes the water itself that is decomposed by the current.

It happens that the chemical changes occurring in electrolysis take place only at the surfaces of the two conductors that dip into the solution where the current enters and leaves. These are the **electrodes.**

Figure 23 shows the apparatus commonly used in the electrolysis of water as a lecture experiment. The U-shaped tube contains water acidified with a little sulfuric acid, to make it conduct better. The electrodes are platinum wires, sealed through the glass walls, near the bottom. When the current passes, hydrogen is liberated at the surface of one electrode and oxygen at the other, displacing some of the dilute acid, which rises in the third vertical tube of the apparatus, and collects in the bulb at the top.

The two products of the electrolysis appear separately at the surfaces of the two electrodes. **Two volumes of hydrogen are produced for every one volume of oxygen.**

Hydrogen is often produced on a commercial scale by the electrolysis of water, using a sodium hydroxide solution, between electrodes of sheet iron. Figure 24 shows a large installation of this kind, producing hydrogen, to be used in hardening vegetable oils (§ 76).

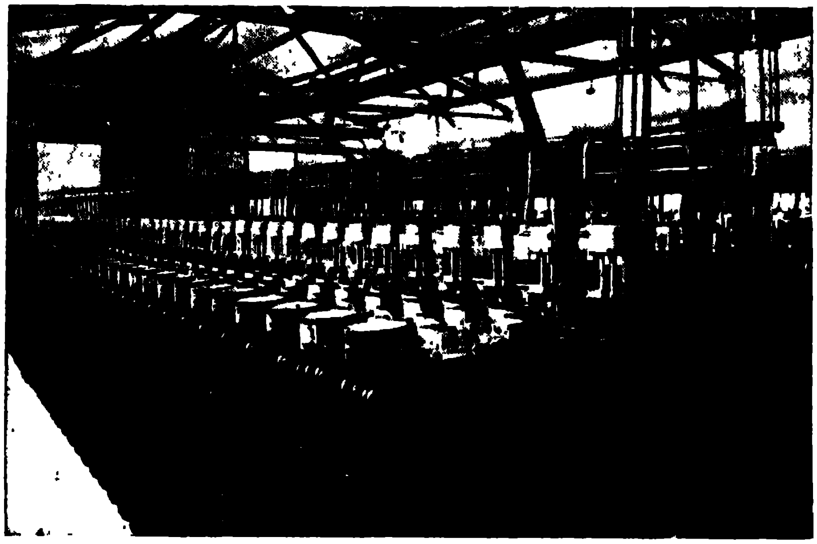


Fig. 24.—Commercial preparation of hydrogen and oxygen by electrolysis of water. This room contains 200 large cells.

66. Decomposition of Water by Metals.—Certain metals, such as sodium and potassium, decompose cold water violently, liberating hydrogen, and forming substances that dissolve to form alkaline solutions (§ 58).

$$2Na + 2H_2O = \underset{\substack{\text{Sodium} \\ \text{hydroxide}}}{2NaOH} + H_2;$$

$$2K + 2H_2O = \underset{\substack{\text{Potassium} \\ \text{hydroxide}}}{2KOH} + H_2;$$

Other metals, such as magnesium or aluminum, decompose water, at an appreciable rate, only if they are finely divided (or alloyed with copper or tin). Even then the water needs to be heated, if the reaction is to be very rapid:

$$Mg+2H_2O=\underset{\text{Magnesium hydroxide}}{Mg(OH)_2}+H_2;$$

$$2Al+6H_2O=\underset{\text{Aluminum hydroxide}}{2Al(OH)_3}+3H_2.$$

In the case of iron, a still higher temperature is necessary. The metal is commonly heated to redness, and the water passed over it in the form of superheated steam.

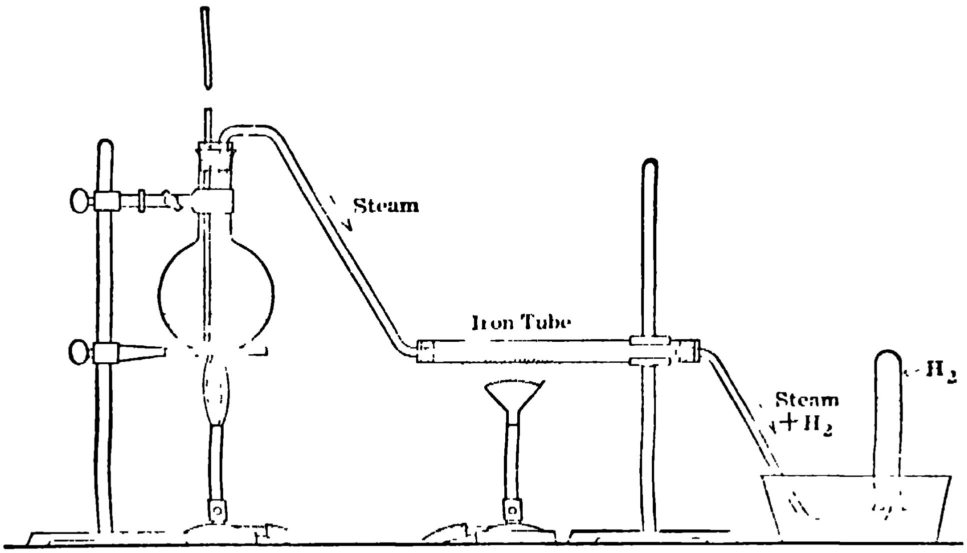


FIG. 25.—Preparation of hydrogen by action of steam on iron.

The apparatus shown in the diagram is the one commonly used on a small scale in the laboratory. Steam is produced by boiling water in the flask, *A*, and is passed through a horizontal, iron tube, *B*, containing iron filings heated to redness The products are hydrogen gas, which is carried away by the steam as fast as formed, and a black powder, *magnetic iron oxide*, Fe_3O_4, that remains behind in the tube:

$$3Fe+4H_2O \rightarrow Fe_3O_4+4H_2.$$

The reaction has sometimes been used for preparing hydrogen for commercial purposes. In a recent modification (Bergius process) liquid water is used at about 300° C., it being possible to reach this temperature without having the water boil, if the latter is retained under sufficient pressure (§ 86).

67. Reversible Reactions Remain Incomplete.—In the reaction just described we heated iron filings in a current of steam, producing magnetic iron oxide and hydrogen. But it is easy to see that this procedure employs much more steam than is really necessary to oxidize all of the iron filings. This is expressed by saying that we used an **excess** of steam.

As the steam passes over the iron the chemical change begins, and continues until all of the iron is oxidized. **A reaction is said to have become complete when it has proceeded until *one or both* the reacting substances have been entirely transformed.**

Under other circumstances this same reaction *never* becomes complete. For example, if water and iron filings are heated together in a closed bomb, rather than in an open tube, the two react to produce a certain amount of iron oxide and hydrogen. But this hydrogen, instead of being swept away by a continuous current of steam, remains in contact with the other product, iron oxide; and at once begins to rob the latter of its oxygen, giving back water and iron.

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O.$$

This reaction is just the reverse of the one by which hydrogen is formed, and of course keeps this from becoming complete, no matter how long the heating is continued.

Reactions are always incomplete under experimental conditions that render them reversible. Such incomplete reactions are formulated with a **double arrow:**

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

We shall meet many examples in what follows.

Such a condition of balance between two opposing forces or processes is called **equilibrium.** A reversible reaction represents a case of **chemical equilibrium.**

68. Conditions under Which Reactions are Complete.—It is evident that a reaction, to be complete, must usually be carried out under conditions such that the products of the reaction are *separated,* before they have a chance to act upon each other, to give back the original reactants.

This happens:

(1) **If one of the products of the reaction happens to be a gas that is permitted to escape as fast as formed.** This was the case in the preparation of hydrogen and oxygen by all the methods that have been described above:

$$2KClO_3 = 2KCl + 3O_2 \uparrow .$$

The arrow pointing upward directs attention to the escape of a gas.

(2) If one of the products of the reaction happens to be **insoluble** in the solvent used. In this case it will separate, and settle to the bottom or float to the top, practically out of contact with the other reaction products. The reverse reaction is thereby prevented.

Thus, when dilute sulfuric acid is added to a solution of barium chloride, $BaCl_2$, a white cloud, consisting of very fine crystals of barium sulfate, $BaSO_4$, is immediately formed. After a time this settles out, leaving above it a clear solution of hydrochloric acid, containing an excess of one of the original reactants.

$$BaCl_2 + H_2SO_4 = BaSO_4 \downarrow + 2HCl.$$

The arrow pointing downward directs attention to the formation and separation of an insoluble solid substance. Such a substance, produced as a result of a chemical reaction, is called a **precipitate.**

69. Water Gas.—When steam is passed through a bed of white-hot coke or anthracite coal, it is reduced to hydrogen, and the carbon of the coke or coal is oxidized to carbon monoxide:

$$H_2O + C = H_2 \uparrow + \underset{\substack{\text{Carbon} \\ \text{monoxide}}}{CO} \uparrow .$$

The mixture of the two gases, hydrogen and carbon monoxide, is called **water-gas.** It is a very important industrial fuel, and within recent years has become the chief commercial source of hydrogen, for the carbon monoxide may be oxidized to carbon dioxide by steam in the presence of an oxide of nickel or iron to serve as a catalytic agent:

$$CO+H_2O=CO_2+H_2.$$

The carbon dioxide thus produced is readily removed, by being dissolved, under pressure, in water. Nearly pure hydrogen then remains.

70. Action of Metals (and Silicon) on Water, in Presence of Sodium Hydroxide.—Zinc, aluminum, silicon, and a number of other elements react vigorously with a warm solution of sodium hydroxide, liberating hydrogen. Since much more hydrogen can be obtained than is present in the sodium hydroxide, the hydrogen is evidently derived chiefly from the water. The sodium hydroxide merely supplies the conditions under which the reaction takes place with reasonable speed.

$$Zn+2H_2O=\underset{\substack{\text{Zinc}\\\text{hydroxide}}}{Zn(OH)_2}+H_2\uparrow;$$

$$Si+4H_2O=\underset{\substack{\text{Silicon}\\\text{hydroxide*}}}{Si(OH)_4}+2H_2\uparrow.$$

The United States Army and Navy use powdered **ferrosilicon** (an alloy of iron and silicon), and a warm 20 per cent solution of sodium hydroxide. The apparatus is often mounted on an automobile truck, forming a portable outfit for filling observation balloons.

How many moles of water are needed to react with each gram-atom of silicon? What weight of water is this? What weight of silicon? What weight of zinc is needed to liberate the same amount of hydrogen as 28 g. of silicon?

71. Action of Metals on Acids.—When zinc is placed in dilute sulfuric acid, it reacts very rapidly, liberating hydrogen gas. The reaction becomes complete (among other reasons) because the hydrogen is permitted to escape as fast as formed. The other product of the reaction is not immediately visible, since it remains dissolved in the water that is present. But if the solution is heated, to evaporate the water, we obtain a white powder, zinc sulfate, $ZnSO_4$.

---

* Otherwise called hydrated silica, or silicic acid.

$$Zn+H_2SO_4=ZnSO_4+H_2\uparrow.$$

In the laboratory, hydrogen is usually prepared by the action of sulfuric acid on zinc in a *Kipp generator* (Fig. 26). The funnel, *F*, fits tightly at *A* and loosely at *B*. Acid added through the funnel rises in the bottom compartment, and comes in contact with zinc in the middle compartment. But when the current of hydrogen thus generated is cut off by turning the stop-cock, the pressure within forces the acid down into the lower compartment, the excess flowing back into the funnel. The chemical action then stops.

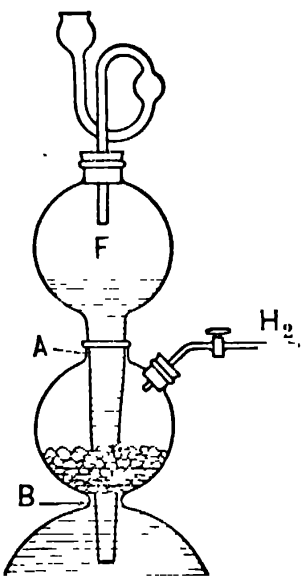


FIG. 26.—Kipp generator.

Many other metals react with acids, liberating hydrogen:

$$Mg+H_2SO_4=\underset{\text{Magnesium sulfate}}{MgSO_4}+H_2\uparrow.$$

$$Ca+\underset{\text{Acetic acid}}{2HC_2H_3O_2}=\underset{\text{Calcium acetate}}{Ca(C_2H_3O_2)_2}+H_2\uparrow.$$

$$Fe+\underset{\text{Hydrochloric acid}}{2HCl}=\underset{\text{Ferrous chloride}}{FeCl_2}+H_2\uparrow$$

In such cases we speak of the metal as *displacing* hydrogen from the acid. The other product (zinc sulfate, calcium acetate, ferrous chloride, etc.), which is formed when a metal displaces a part or all of the hydrogen of an acid, is called a **salt.** Each salt is named from the acid from which it is thus derived.

Sulfates are salts of sulfuric acid;
Acetates are salts of acetic acid;
Nitrates are salts of nitric acid;
Phosphates are salts of phosphoric acid;
Chlorides are salts of hydrochloric acid.

A salt often contains one or more **groups of atoms,** originally present in the acid, and remaining unaffected when the hydrogen of the acid is displaced by a metal. We call these **non-metallic radicals,** or **electronegative radicals.** Important non-metallic radicals are:

Sulfate radical, SO_4, contained in sulfuric acid and all sulfates.

Acetate radical, $C_2H_3O_2$, contained in acetic acid and all acetates.

Nitrate radical, NO_3, contained in nitric acid and all nitrates.

Phosphate radical, PO_4, contained in phosphoric acid and all phosphates.

Hydroxyl radical, OH, contained in water, HOH, and all hydroxides.

Note that radicals are not substances, having separate existence in themselves, but are merely parts of molecules. If a molecule contains more than one radical of a given kind, parentheses are used, as in $Ca(C_2H_3O_2)_2$, which contains two acetate radicals.

Draw up a table in two columns, the first giving formulas of the acids named above, the second, formulas of salts derived from the acids by replacing each hydrogen atom by a sodium atom. Point out the radical in each case, by underlining.

Write formulas of mercuric nitrate (two nitrate radicals), chromic acetate (three acetate radicals), ferric hydroxide (three hydroxyl radicals). To what class of substances does the last-named compound belong?

§§ 101, 118 may be introduced here, if desired.

72. The Electrochemical Series.—Not all metals react with all acids; and when they do, the product is not always hydrogen. A practical guide is to be found in the **Electrochemical Series,** which is a list of metals arranged in the order of **decreasing chemical activity.** Each given metal is more active than those below it, by which we mean that it will react *more rapidly* or *more readily* with water or dilute acids. Thus, magnesium is more active than aluminum, and the latter more active than zinc.

Potassium	K
Sodium	Na
Calcium	Ca
Magnesium	Mg
Aluminum	Al
Manganese	Mn
Zinc	Zn
Chromium	Cr
Iron	Fe
Nickel	Ni
Tin	Sn
Lead	Pb
HYDROGEN	H
Copper	Cu
Bismuth	Bi
Antimony	Sb
Mercury	Hg
Silver	Ag
Platinum	Pt
Gold	Au

1. Metals near the top of the series (K, Na, Ca) are so active that they readily displace hydrogen from water, even at room temperature. Those somewhat lower down (Mg, Al, Zn) still do so with reasonable rapidity when the water is heated, or in the presence of sodium hydroxide. Those still lower down (Fe, Sn) act on steam but require temperatures near a red heat. Those below hydrogen (Cu, Hg, Ag, Pt) do not decompose water appreciably, at any temperature.

2. Metals displace hydrogen from acids much more readily than they do from water. Those near the top of the series react with acids with dangerous violence. It would be hazardous to place metallic sodium or potassium in most acids. As we descend in the series, the violence of the action decreases, and the elements below hydrogen do not displace hydrogen, even from the most active acids.

3. Concentrated sulfuric acid, and either dilute or concencentrated nitric acid are classified as **oxidizing acids.** These react readily with most metals, even with those below hydrogen in the electrochemical series; but the reaction produces other gases than hydrogen.[*] Thus, copper dissolves in dilute nitric acid to produce *nitric oxide* gas (NO); and silver dissolves in hot, concentrated sulfuric acid to produce sulfur dioxide gas (SO_2). Other products, in each case, are water and a salt.

In which of the following cases will the metal probably react, and in which of these will hydrogen probably be liberated?

Tin and hydrochloric acid.
Copper and dilute sulfuric acid.
Silver and phosphoric acid.
Manganese and concentrated nitric acid.
Iron and acetic acid.
Copper and concentrated sulfuric acid.
Silver and dilute nitric acid.
Magnesium and hydrochloric acid.

Which of the preceding reactions will probably be the most vigorous, under like conditions?

73. Physical Properties of Hydrogen.—The most striking physical property of hydrogen is its extreme *lightness.* It is not much more than a fifteenth as heavy as air, and only a sixteenth as heavy as oxygen. It dissolves very slightly in water, and can be liquefied only at very low temperatures, best in connection with very high pressures (−253° C., at 20 atmospheres).

Hydrogen is absorbed very rapidly, and in enormous quantities, by finely divided platinum or palladium. One volume of palladium will absorb as much as 500 volumes of hydrogen. The absorbed hydrogen is in a very active condition, and is at once oxidized to water, if exposed to air or oxygen.

74. Direct Union of Hydrogen with Oxygen. Law of Gay-Lussac.—Chemically, hydrogen is distinguished **by the fact that it combines with oxygen to form water.**

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[*] Very dilute nitric acid, with some of the most active metals (Mg) gives considerable hydrogen, and other gaseous products.

Hydrogen generated by the action of zinc on dilute sulfuric acid in a flask or Kipp generator (§ 71) is first freed from water by being passed through a horizontal tube (Fig. 27) filled with granular calcium chloride, a substance remarkable for its ability to absorb water. After the air originally present in the flask has been displaced by the escaping hydrogen, the jet may be lit The flame is commonly yellowish, from sodium contained in the glass tip, but with a metal tip is practically colorless. If the flame is covered with a bell-jar moisture collects on this, and soon trickles off as visible drops of water.

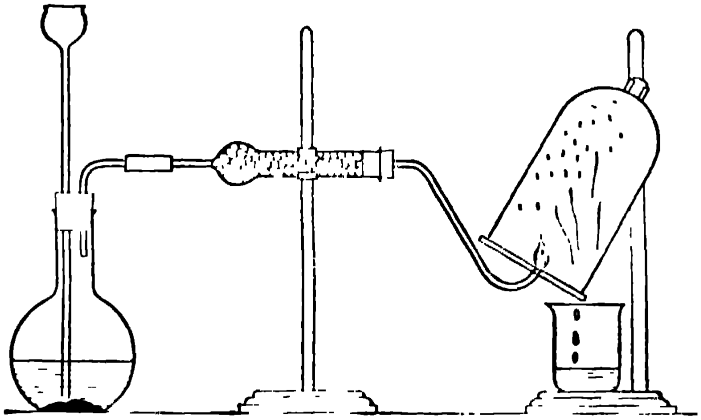

Fig. 27.—Burning hydrogen under a bell jar.

Not only does hydrogen burn in oxygen, but oxygen in hydrogen.

This is shown in Fig. 28, in which a cylinder of hydrogen has been ignited, and a tiny jet of oxygen, from a cylinder of that gas, thrust up into it. Below we have hydrogen burning in air, and above that a jet of oxygen, burning in hydrogen. In both cases the product is water. If the upper jet goes out the current of oxygen must instantly be cut off. Why?

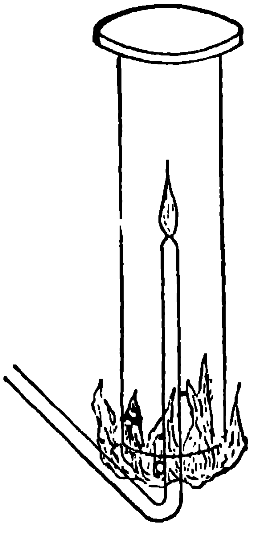

Fig. 28.

Hydrogen and oxygen combine to form water in the proportions in which they are produced from water by electrolysis (§ 65): exactly* **two volumes of hydrogen to one volume of oxygen.** If the water vapor that is produced is measured under the same conditions, it will occupy the same volume as the hydrogen did (two volumes).

We have here an illustration of the **Law of Gay-Lussac**: The volume of all gases transformed or produced in any given chemical reaction are simply related to each other. ("Simply related" means bearing to each other a ratio of small whole numbers; such as 1 : 2; or 3 : 4; or 5 : 7.)

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*Some departure from an exact ratio can be detected in very accurate experiments; but this no longer happens if correction is made for the fact that neither of the two gases obeys the Laws of Charles and Boyle exactly (§ 20).

Further illustrations of this law are as follows:

1 volume of hydrogen	reacts with	1 volume of chlorine	to form	2 volumes of hydrogen chlor-
1 volume of nitrogen	reacts with	3 volumes of hydrogen	to form	2 volumes of ammonia
2 volumes of carbon monoxide	react with	1 volume of oxygen	to form	2 volumes of carbon dioxide
2 volumes of acetylene	react with	5 volumes of oxygen	to form	4 volumes of carbon dioxide and 2 volumes of water vapor

Note that the total volume occupied by the mixture of gases sometimes changes as a result of the reaction, and sometimes does not. The important fact is that there are simple ratios between the volumes of all the reactants and resultants that happen to be gases. The law does not apply to liquids or solids.

By what fraction of its original volume does each of the above mixtures expand or contract, as a result of the chemical reaction?

The Law of Gay-Lussac is a necessary consequence of the **Principle of Avogadro** (§ 22). For only whole numbers of molecules are concerned in chemical reactions; and in every case some *small whole number* of molecules of one kind reacts with some *small whole number* of another kind. Then, since equal numbers of molecules of all gases occupy equal volumes, the *volumes* must be in the same ratios as the *molecules* a ratio of small whole numbers.

What number of molecules of each of the other gases is transformed or produced if 5 molecules of nitrogen are combined with hydrogen?

How many moles of oxygen are needed to burn one mole of acetylene, to form carbon dioxide and water vapor.

75. Hydrogen a Reducing Agent.—Read § 55. Substances, like ozone and sodium peroxide, that readily oxidize other substances, are called **oxidizing agents.** Hydrogen has exactly the contrary property: it will abstract oxygen from many substances containing it. This is reduction (§ 55), and hydrogen is accordingly a **reducing agent.**

A copper crucible, heated in the air, becomes covered with a black coating of copper oxide, CuO. But on exposing it to a current of hydrogen (Fig. 29), while it is still hot, the color of copper reappears:

$$CuO+H_2=Cu+H_2O.$$

76. Uses of Hydrogen.—Hydrogen is used:

1. In the oxy-hydrogen blowpipe (welding and cutting metals, § 59).

2. In hardening animal and vegetable fats and oils. Such substances as whale oil, cottonseed oil, and cocoanut oil, if heated in contact with a catalyzer of finely divided nickel, readily absorb hydrogen gas, uniting with it chemically to form a solid fat. Soap is often made from such hardened material. Various brands of oleomargarine and certain familiar lard substitutes contain considerable amounts of hydrogenated cottonseed oil and cocoanut oil. At present, many hundred thousand tons of oils are thus **hydrogenated** every year, to produce solid fats.

3. In preparing ammonia (§ 284). Nitrogen and hydrogen are made to combine directly to form ammonia, under the influence of finely divided platinum, which serves as a catalyzer.

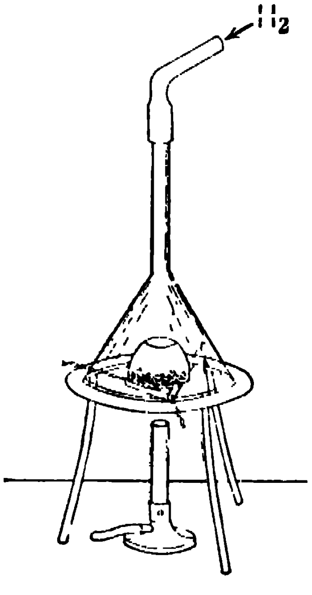
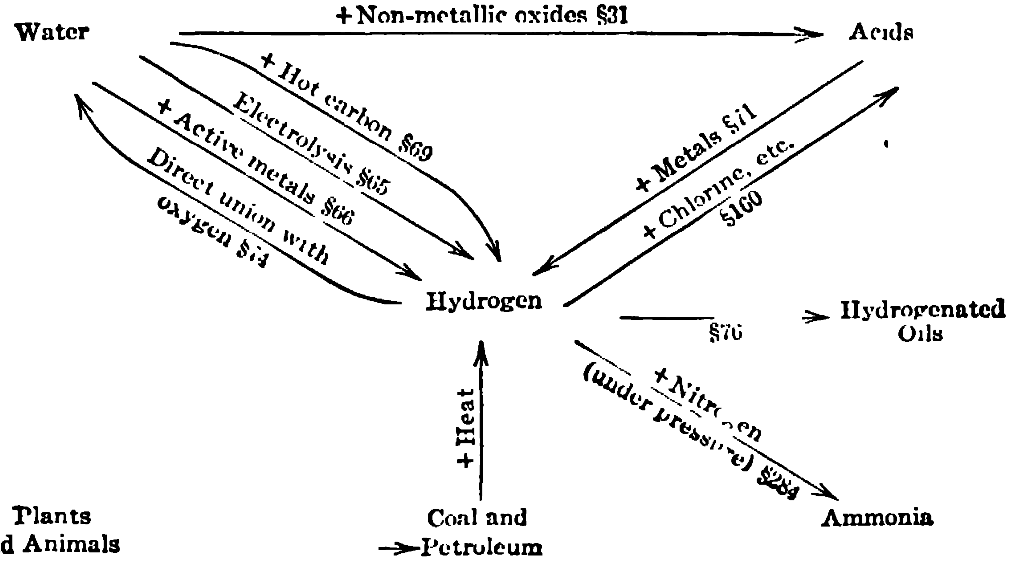


FIG. 29.—Reducing copper oxide in a current of hydrogen.

4. Very recently, carbon monoxide and hydrogen have been made to combine directly, in the presence of certain catalyzers, to form methyl alcohol or **methanol,** CH_3OH. This is an important solvent for varnishes and lacquers, and may eventually compete with gasoline as a fuel for automobiles.

5. In filling dirigible balloons. Helium, condensed from Texas and Oklahoma natural gas by liquid air machines, has the advantage of being non-inflammable, but has not quite the buoyant effect of hydrogen, and there is difficulty in getting enough of it.

77. Graphical Summary.



Electrolysis § 65

Salts and Radicals § 71

Electrochemical series

EXERCISES

1. Formulate several reactions between metals and water. Name and describe the product in each case.

2. Under what circumstances does a reaction usually become complete, and under what circumstances does it remain incomplete? Illustrate.

3. Describe and sketch an apparatus by means of which it should be possible to reduce magnetic iron oxide completely to metallic iron, by means of hydrogen. Formulate the reaction.

4. Formulate the reaction that takes place when magnesium dissolves in an *excess* of acetic acid. What *two* dissolved substances are contained in a solution thus prepared?

5. Summarize the principal methods for preparing hydrogen, with a formulation to illustrate each. Name the substance, other than hydrogen, produced in each case.

6. Under what conditions will metals usually react with acids, liberating hydrogen?

7. If a reaction takes place in any of the following cases, state what substances are formed; if no reaction takes place, state why:

(*a*) Sodium on water.
(*b*) Iron on steam.
(*c*) Copper on steam.
(*d*) Copper on dilute acetic acid.
(*e*) Zinc on phosphoric acid.
(*f*) Copper on nitric acid.
(*g*) Silver on hot concentrated sulfuric acid

8. In a plant for hydrogenating vegetable oils (§ 76) a certain oil is found to absorb 2 per cent of its weight of hydrogen. What weight of water must be electrolyzed to furnish hydrogen for a ton of oil?

9. With the aid of the text, checked by the dictionary, draw up formal definitions for the following: Electrolysis, electrolyte, electrode, excess, equilibrium, precipitate, salt, radical.

10. Explain the connection between Avogadro's Principle and the Law of Gay-Lussac.

11. When iodine vapor, I_2 (violet) is heated with hydrogen in a closed tube, a certain amount of hydriodic acid, HI (colorless) is formed. But the violet color never disappears entirely, no matter how long the tube is heated. Explain. Formulate the reaction in accordance with your explanation.

12. Write and balance an equation for the synthesis of methyl alcohol from carbon monoxide and hydrogen. What volume of carbon monoxide is needed for each cubic meter of hydrogen? What law does this illustrate?

CHAPTER VI

WATER AND HYDROGEN PEROXIDE

78. Occurrence of Water.— Water covers three-fourths of the earth's surface to an average depth of three miles. The atmosphere contains enormous quantities as *water vapor*— often as much as 50,000 tons in the air over a square mile of the earth's surface, at summer temperatures. All our food contains water, from about 60 per cent in lean meat to as much as 95 per cent in watery fruits. Even the solid rocks of the earth's crust hold water in chemical combination with different mineral substances— so much of it indeed that most of the land areas of the earth would be submerged if it were suddenly returned to the ocean.

Water owes much of its importance in chemistry to the fact that it is so often used as a **solvent** to dissolve other things; for many chemical reactions take place most readily when the substances concerned are first dissolved in water and the solutions mixed (§ 212).

79. Hydrates. - A crystal of copper sulfate, though apparently dry, is actually more than one-third water, in chemical combination with copper, sulfur, and oxygen. If the crystal is heated in a test-tube, this water is driven off in part and condenses as visible moisture in the upper part of the tube.

Crystals containing such chemically combined **water of crystallization,** better called **water of hydration,** are known as **hydrates.** An interesting fact is that **every hydrate contains an invariable percentage of water of hydration,** and hence may be represented by a definite chemical formula. The blue crystals of copper sulfate hydrate, for example, have the formula $CuSO_4 \cdot 5H_2O$.* When these are gently heated, they crumble, lose water, and form a nearly white powder, anhydrous copper sulfate, $CuSO_4$. (An **anhydrous salt** is one containing no water of hydration.)

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* The period is read "point," not "times" It is used to direct attention to the fact that the water of hydration may be driven off by heat, often leaving the rest of the molecule unaltered.

We have noted that many of the minerals of the earth's crust contain considerable quantities of water of hydration. The process of hydration is still going on, and in the very distant future may appreciably diminish the volume of the ocean.

80. Efflorescence and Deliquescence.—(Review § 29.) If a crystal of a hydrate is introduced into the evacuated space above the mercury column, at the top of a barometer, it will yield up a little water vapor. This will depress the level of the mercury, by an amount which is *constant for each kind of crystal*, at any given temperature. This result shows that the water of hydration in each crystal possesses a definite vapor pressure, which measures its tendency to escape from combination with the salt.

Now, it sometimes happens that this vapor pressure of the water of hydration in a crystal is *greater* than the vapor pressure of the moisture in the air in which the crystal is placed. In this case, the crystal gradually yields up water to the atmosphere, and finally crumbles to an anhydrous powder. Such crystals are said to be **efflorescent.** Sodium sulfate hydrate, $Na_2SO_4 \cdot 10H_2O$, effloresces in ordinary air.

In other instances, the vapor pressure of the water of hydration is *less* than that of the moisture in the surrounding atmosphere. In this case the crystal gains moisture from the air, and finally dissolves in it to form a solution. Such crystals are said to be **deliquescent.** Thus, table salt commonly grows moist in damp weather, owing to the presence in it of small amounts of deliquescent impurities. Anhydrous calcium chloride, $CaCl_2$, is so very deliquescent that it is often used for drying gases, and for settling dust on roads. It must be understood, however, that whether a hydrate will effloresce or deliquesce depends not only on the vapor pressure of its water of hydration, but also on the humidity of the atmosphere. In perfectly dry air, all hydrates effloresce. In fully saturated air, all substances of measurable solubility deliquesce.

81. Common Impurities in Water.—Water dissolves a part of nearly everything it meets. Well water or river water commonly contains salts of **calcium, magnesium, iron, potassium,** and **sodium,** together with organic matter from decaying leaves and twigs, small amounts of ammonia, and gases from the atmosphere. In addition, the water may carry such **suspended impurities** as fine clay and sand, fragments of vegetation, and microscopic organisms of all sorts, including bacteria.

Calcium and magnesium salts are said to make water **hard.** By this we mean that they react chemically with soap, altering it into substances insoluble in water (§ 459). Hard water thus requires more soap to produce a lather. It is objectionable in steam boilers because the calcium and magnesium salts often separate when the water is heated, forming a **scale,** which coats over the walls of the boiler-tubes, and prevents heat from being transmitted to the water that surrounds them. The result is a great waste of fuel, and sometimes an explosion. Iron salts in water give it an objectionable taste, and cause spots of rust to appear on clothing during laundering. The methods of treating industrial water to free it from such impurities are discussed hereafter (§§ 460, 462).

82. Water for Domestic Use.—Public health is largely dependent on supplies of water of proper quality for domestic use. Natural waters but rarely contain mineral substances of a kind or quantity to be injurious to health; it is disease-producing microörganisms that are to be feared. Typhoid and cholera have been proved very definitely to be chiefly caused by infected water supplies.

In this respect the cities of the Middle Ages were in a deplorable condition, and it is no wonder that pestilences carried off whole populations. Even in modern times, conditions have been far from satisfactory; and until very recently most modern cities have had supplies of domestic water far inferior to that of ancient Rome or the principal Roman colonies. Unfortunately, water that is clear, cool, and sparkling is often highly contaminated. It may be clear, if it has filtered through a little soil; cool, if it has not penetrated the earth to great depths; sparkling, and of pleasant taste, if it is charged with carbon dioxide gas. In spite of all this, it may contain millions of bacteria per cubic centimeter. Under modern conditions, in most parts of the world, every surface well should be regarded as subject to contamination. Infection will percolate through the soil for hundreds of feet, in some instances, from a cess-pool or other source. Yet even to-day, in many country districts and a few towns, unprotected surface wells furnish most of the domestic supply.

Water from artesian wells, properly cased to prevent surface water from getting into them, is practically safe. The only safe substitute is water that has been treated to destroy disease germs. So well have modern methods been developed, under the control of the chemist and bacteriologist, that it would be possible to prepare a perfectly safe and potable drinking water from sewage. If the water supply is very turbid, it is commonly treated with small amounts of **calcium hydroxide** (slaked lime) and alum or **aluminum sulfate.** These interact to form sticky particles of aluminum hydroxide, to which the clay and sand tend to cling, forming larger flocks, which settle readily.

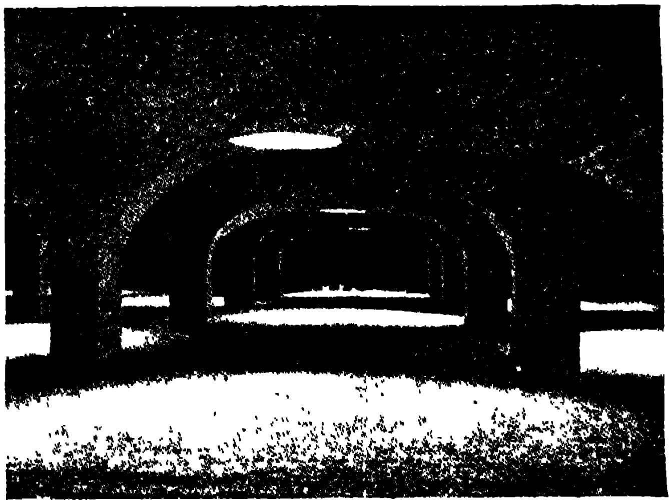

FIG. 30.—A filter bed at Ashland, Wis. The brick archways support a vaulted roof, covered with earth, to prevent freezing and discourage the growth of aquatic plants. The filter bed (here shown without its covering of water) is of fine sand, about three feet deep. Beneath this is a layer of gravel, and tile drains to carry away the filtered water. Ingenious devices have been invented to remove, wash, and replace the upper portion of the sand layer, when it has become clogged with muddy material.

After settling, the partially clarified water is filtered through a bed of fine sand (Fig. 30). This removes most of the remaining sediment; and presently the grains of sand become covered with a jelly-like coating of harmless bacteria (zoöglœa), which entangles and retains most of the disease-producing bacteria. In addition, if the filtering is intermittent, or carried out in the presence of a reasonable supply of air, other beneficent bacteria oxidize and destroy objectionable organic matter.

To destroy the remaining bacteria, the filtered water is next treated with a very small amount of chlorine gas (metered from a cylinder of liquid chlorine). It may then be sprayed into the air to oxidize and remove objectionable odors and give it a pleasant taste. In Europe, ozone is frequently used instead of chlorine; and ultraviolet light, in small installations, has been found to possess sufficient germicidal effect.

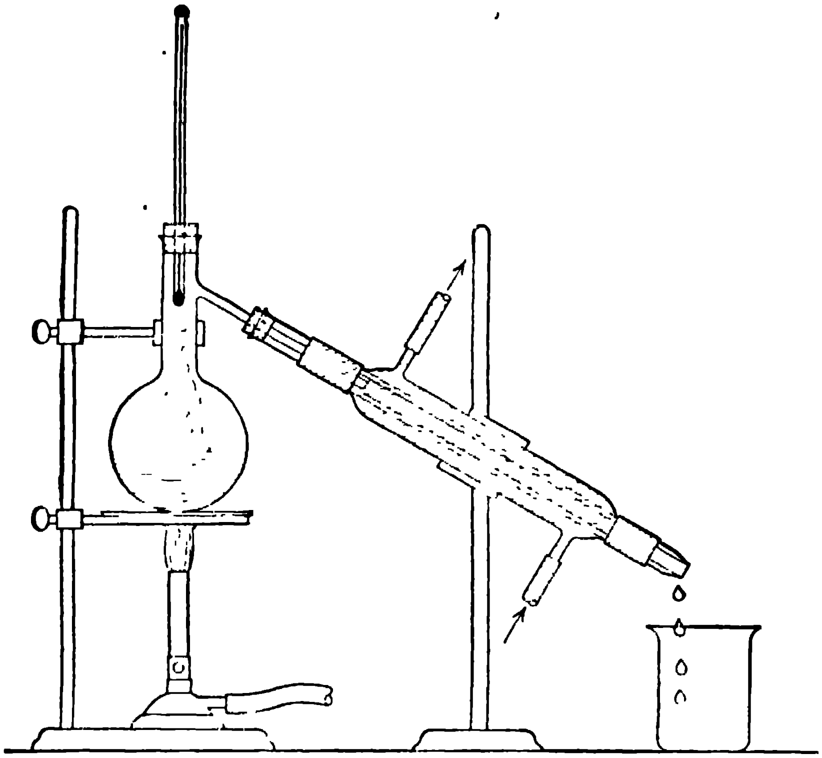

FIG. 31. —Distillation.

83. Distillation.—Water that is to be used in the chemical laboratory or for certain industrial purposes must first be purified by distillation, which removes most of dissolved impurities. We have already noted, however, (§ 10) that certain volatile impurities (such as ammonia gas and carbon dioxide gas) pass over with the distillate. If it is desired to remove these, the distilled water is treated with an oxidizing agent (such as potassium permanganate) to destroy the ammonia, and is then redistilled, under such conditions as will prevent carbon dioxide gas from entering from the air. In such cases, the inner tube of the **condenser**

(Fig. 31) is commonly of tin, silica (§ 395), or at least hard glass, since ordinary soft glass dissolves appreciably in water.

Though distillation is most easily employed to separate a **volatile** liquid from **non-volatile** impurities, still, two liquids, both of which are volatile, may sometimes be separated, almost or quite completely, by repeated distillation. In such cases the vapors first passing through the condenser (i.e., the first portions of the **distillate**) contain more of the more volatile constituent than the original mixture. By thus separating the material into two or more **fractions,** and redistilling these, practically complete separation can often be effected. This is **fractional distillation.**

84. Water Has Its Greatest Density at 4° C.—A number of the purely physical properties of water, such as its density, freezing point, and boiling point, are of such importance in chemical work as to deserve mention here. Water has its greatest density at 4° C.; and on either heating or cooling from this temperature, expands slightly. This is the reason why 4° C. was specified in our definition of the milliliter (§ 33).

85. Freezing and Melting.—If a test-tube of water containing a thermometer is placed in a mixture of salt and crushed ice, and the water slowly stirred, the temperature will fall regularly, and may even descend several degrees below zero. But if the experiment is carried out with certain necessary precautions it will be noticed that **when freezing finally sets in the temperature at once begins to rise.** This fact proves that **freezing liberates heat.** When the temperature has come back to 0° C., no further rise takes place.

This interesting behavior is shown very clearly in the *freezing curve* in the annexed sketch: First a fall (*AB*) during five minutes' time, from 10° C. to − 5° C.; then a rapid rise (*BC*), during half a minute, to 0° C.; then constant temperature (*CD*) during the progress of the freezing, for ten minutes more; and finally another drop in temperature (*DE*) after the thermometer bulb has become surrounded with a solid cake of ice.

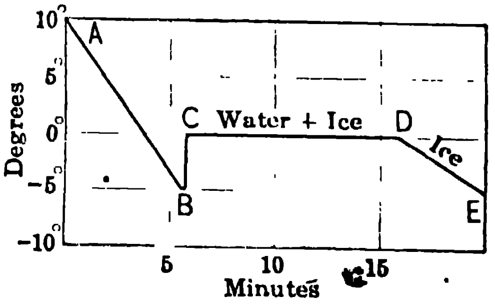

Fig. 32.

The initial descent below 0° C. is known as *supercooling*. It is favored by using water that is free from dust or dissolved air, but may be overcome by violent stirring or by the introduction of a small crystal of ice from without. No similar delay is observed when ice is heated: The temperature rises to 0° C.; then melting begins promptly, heat being absorbed as fast as it arrives from the outside source; finally, when the ice is all melted, the temperature mounts once more.

These experiments prove that zero degrees Centigrade is the only temperature at which ice and liquid water can remain in contact with each other indefinitely, at atmospheric pressure. This is accordingly the **freezing point** of water. (The freezing point of any substance is the temperature at which the liquid and solid forms of the substance may remain indefinitely in equilibrium with each other, under standard atmospheric pressure.)

Though pure water begins to freeze at 0° C., if supercooling is prevented, **the addition of any other substance to water always lowers its freezing point.** Thus, sea-water begins to freeze several degrees below zero. The **melting point** of ice in contact with pure water is the same as the freezing point of pure water.

86. Boiling.—The vapor pressure of water increases rapidly as its temperature increases. In the end, if the water is in an open vessel, the vapor pressure becomes equal to the external pressure due to the weight of the atmosphere (15 lbs. per sq. in. = 76 cm. of mercury). Evaporation, from this moment on, instead of proceeding quietly from the surface of the liquid, may take place in its interior. Bubbles of vapor thus formed within the body of the liquid rise rapidly to its surface, and we say that the liquid boils.

The **boiling point of any liquid is the temperature at which its vapor pressure becomes equal to the external pressure.**

If the external pressure is reduced by an air pump, or by transporting the liquid to the top of a high mountain, the boiling point is correspondingly lowered. **Unless otherwise specified, the boiling point of a liquid is assumed to be under the standard pressure of 760 mm.**

The fact that water boils at a lower temperature in a partial vacuum than it does under atmospheric pressure is put into practical use in the evaporation of milk, sugar, syrup, and other solutions. Such liquids would be injured if heated to the temperature needed to boil them at ordinary atmospheric pressure, but may be concentrated or evaporated entirely to dryness in a partial vacuum (Fig. 33). With a pressure cooker, or *autoclave*, on the other hand, the boiling point of a liquid may be raised. This principle is applied in preparing glucose syrup from starch and in many other industries.

87. Critical Temperature.—Though water heated in a closed vessel cannot boil, more and more of the liquid does evaporate into the closed space as the temperature is raised. Thus the *vapor* gradually becomes more and more dense, while the *unevaporated liquid* expands and becomes less and less dense.

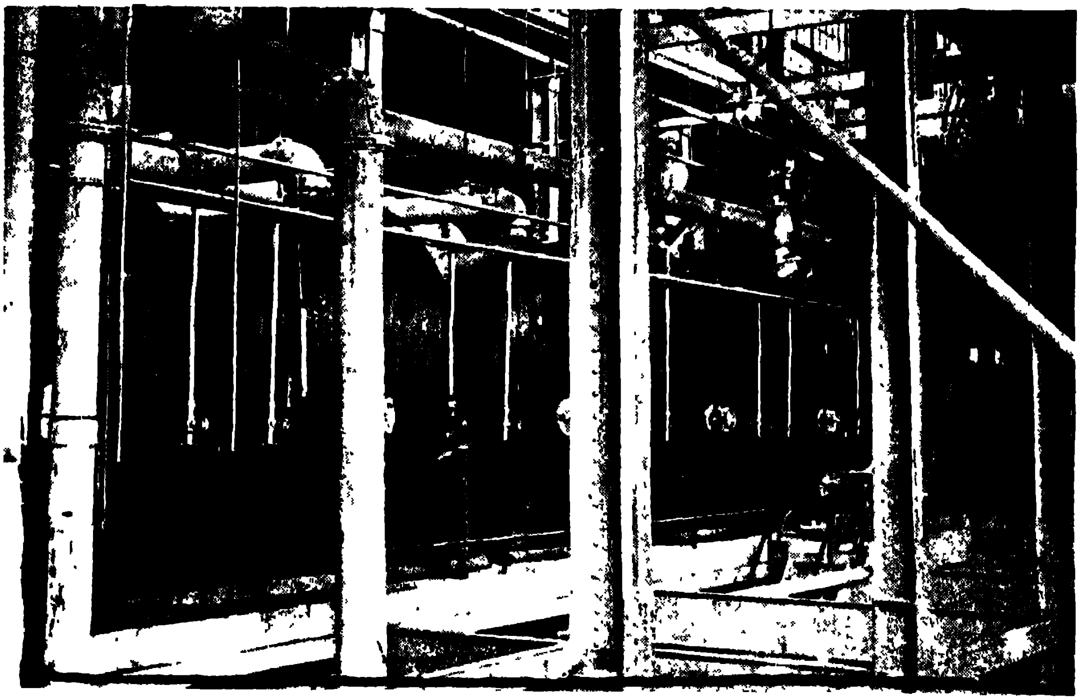

FIG. 33.—A battery of vacuum-pans in a beet sugar factory.

Finally, at a temperature of 365° C., liquid and vapor actually acquire the same density. At this moment they can mix with each other, and the surface dividing liquid from vapor suddenly disappears! The temperature at which this happens is called the **critical temperature.** It is the **highest temperature at which a liquid can retain a definite bounding surface, separating it from its own vapor.** But whether water above its critical temperature should be considered as a liquid of very low density, or as a vapor of exceedingly high density, or as a mixture of the two, it is impossible to say.

88. The Chemical Properties of Water.—Water often reacts chemically with other substances. The following cases are the most important:

1. It **combines directly** with metallic oxides (§ 58), non-metallic oxides (§ 58), and salts (§ 79).

What name is given to the product in each of these three cases? Write equations to illustrate. How many moles of water are combined with one mole of anhydrous copper sulfate to form copper sulfate hydrate? What actual weights (in grams) of water and copper sulfate hydrate are thus represented? From this, calculate the percentage of water in copper sulfate hydrate.

2. It reacts with active metals, which displace a part of its hydrogen, forming a metallic hydroxide (base); or all of its hydrogen, forming a metallic oxide (§ 66).

Give an equation to illustrate each of these cases. Name three metals that will not react appreciably with water, even at high temperatures.

3. It reacts with a few salts in such a way as to form an acid and a base. Thus, when a dilute (yellowish) solution of ferric chloride is boiled for a long time, hydrochloric acid escapes with the steam, and a deep red colloidal solution (§ 91) of ferric hydroxide is left behind:

$$FeCl_3+3HOH=Fe(OH)_3+3HCl\uparrow.$$

Reactions of this kind are said to be cases of **hydrolysis,** and the salt is said to be hydrolyzed. We shall presently (§ 113) explain why some salts are readily hydrolyzed, while others are not.

Tell what products are formed when magnesium sulfate is hydrolyzed. Write equation. (The necessary formulas have been given previously.)

89. The Quantitative Synthesis of Water.—By **synthesis** we mean the formation of a complex substance by interaction (commonly, direct union) of simpler ones. Thus, the organic chemist synthesizes the complex molecules of dyestuffs and perfumes from the comparatively simple molecules of substances found in coal-tar.

By a **quantitative synthesis** we mean one accomplished in such a way as to determine the exact proportions (commonly, by weight) in which simpler substances combine to form a complex one. Chemists have expended years of effort, during more than a century, on the quantitative synthesis of water, to determine the exact proportions, by weight, in which hydrogen and oxygen combine to form water. This seemed worth while, because the result could be made to reveal the relative weights of the atoms of hydrogen and oxygen. The two most accurate determinations have been made by American chemists.

1. The apparatus of *W. A. Noyes* is shown in the accompanying figure. Copper oxide was placed in the bulb, *A*, and the apparatus exhausted and weighed. Pure hydrogen was then slowly admitted through *C*, while the bulb was heated. Oxygen contained in the copper oxide united with the hydrogen to form water. This water was condensed to ice in the vertical portion, *B*, placed in a freezing mixture. After a time the stop-cock, *E*, was closed, and the apparatus cooled and weighed. The increase in weight was the weight of hydrogen taken. The water was finally driven out of the apparatus by warming *B* and *A*. The total weight was then less than at first, the deficiency being the weight of oxygen yielded up by the copper oxide to combine with the hydrogen. The mean of twenty-four experiments gave 1.00787 parts of hydrogen to 8 parts of oxygen.

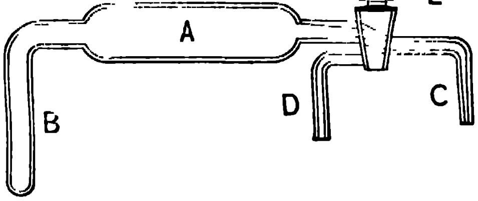

FIG. 34.

2. The wonderfully painstaking experiments of *Morley* occupied more than twelve years. Hydrogen and oxygen gases were weighed separately and permitted to come together in a special weighed apparatus provided with platinum terminals between which electric sparks passed. These sparks caused the two gases to combine to form water, which was condensed and *weighed.* The mean of twelve experiments gave 1.00762 parts of hydrogen to 8 parts of oxygen.

Chemists have adopted the ratio 1.008 (parts by weight of hydrogen) : 8 (parts by weight of oxygen), obtained by rounding off the results of the experiments described above.

90. Hydrogen Peroxide. The Law of Related Composition.— The compound called hydrogen peroxide contains just twice as much oxygen, for a given weight of hydrogen, as does water. The two compounds thus illustrate the **Law of Related Composition** (sometimes called the Law of Multiple Proportions): **A fixed weight of some one element** (say hydrogen) **may often be made to combine with several different weights of another element** (say oxygen) **to form a corresponding number of different compounds. When this happens, the different weights of the second element are all simply related to each other.** ("Simply related" means bearing to each other a ratio of small whole numbers; such as 1 : 2; or 3 : 4; or 5 : 7.)

Work the last three problems at the end of this chapter.

The fact that hydrogen peroxide contains twice as great a weight of oxygen as does water, for a given weight of hydrogen, suggests that each molecule of hydrogen peroxide contains twice as many *atoms* of oxygen as a molecule of water. Then, if water is H_2O, hydrogen peroxide must be H_2O_2. Hydrogen peroxide cannot be made by direct union of hydrogen and oxygen, but is prepared indirectly, for example by treating a metallic peroxide with a cold, dilute acid:

$$BaO_2 + H_2SO_4 = BaSO_4 \downarrow + H_2O_2.$$

The dilute solution of hydrogen peroxide thus obtained decomposes slowly, liberating oxygen gas, even at room temperature; it decomposes more rapidly when heated, or in the presence of certain catalyzers, or when exposed to sunlight:

$$2H_2O_2 = 2H_2O + O_2 \uparrow .$$

Hydrogen peroxide is an oxidizing agent. It oxidizes and thus decolorizes many colored substances, and is therefore used for bleaching silk, wool, and hair. As an antiseptic, it has been much overrated.

EXERCISES

1. Explain the relation between aqueous tension, atmospheric pressure, and boiling point

2. Describe what happens when water is heated in a closed steel bomb to higher and higher temperatures. Is there a sudden increase in pressure at any one temperature?

3. How many cubic centimeters of liquid water must be decomposed to furnish 100 g of oxygen?

4. How many milligrams of hydrogen gas must be burned to produce a cubic centimeter of liquid water?

5. Tell what circumstances determine whether a crystal will deliquesce or effloresce when exposed to the air.

6. Distinguish between boiling and evaporation.

7. Sketch and interpret a freezing-point curve.

8. What impurities in water unfit it for industrial use, and why?

9. What is meant by each of the following: hydrate, anhydrous salt, hydrolysis, synthesis, analysis, density, distillation, fractional distillation, distillate, volatile substance, suspension?

10. Write and balance an equation for the formation of hydrogen peroxide and sodium acetate by the action of acetic acid on sodium peroxide.

11. In what respect are ozone and hydrogen peroxide alike? What fraction of the oxygen in ozone is most readily available for oxidizing other substances? What fraction of that in hydrogen peroxide?

12. Show that the following substances obey the Law of Related Composition:

	Parts of A	Parts of B
Compound No. 1 . .	$10\frac{1}{2}$	3
Compound No. 2	10	$3\frac{1}{3}$
Compound No. 3 . .	$10\frac{5}{9}$	$2\frac{1}{9}$

(*Suggestion*: Find how many parts of A, in each compound, are combined with 1 part of B.)

13. Yellow lead oxide contains 103.6 parts by weight of lead, for every 8 parts by weight of oxygen. Red lead oxide contains 90.76 parts of lead, for every 9.34 parts of oxygen. Find how many parts of lead (to three decimal places), in each compound, are combined with one part of oxygen. Then show that these results illustrate the Law of Related Composition.

14. In the preceding problem, find how many parts of oxygen (to four decimal places), in each compound, are combined with one part of lead. Then show that these results also illustrate the law.

Topics for Individual Reports

See references in Appendix *K*.

A. What is the source of the water supplied to your campus? Outline the process used in purifying it. If it differs from that outlined in the text, try to find out why.

B. Similarly, discuss the source and method of purification of the water used in your own home.

C. Find out something about the cost of treating water by some of the standard methods.

D. For what impurities does a chemist generally test drinking water, and why?

E. Explain what geological formation is favorable to artesian wells.

F. In one of the reference books on enzymes find out something about the occurrence and properties of the enzyme called *catalase*.

CHAPTER VII

SOLUTIONS

91. Coarse and Fine Mixtures.—Such things as sand, Graham flour, or milk, are obviously **mixtures,** for in them we may easily distinguish particles of different kinds: grains of different colors; flakes of bran among granules of starch; or droplets of cream, of microscopic size, suspended in watery fluid. Such materials are always *variable*, both in their properties and their chemical composition, (§ 13), presumably because different samples vary in the proportions in which their chief ingredients are intermingled.

Certain mixtures are barely recognizable as such when examined with a powerful microscope. Others contain particles too fine to be detected by the best microscopes, but still recognizable with the aid of an ultramicroscope, § 94. Finally, we have mixtures which appear to be perfectly homogeneous by all tests, yet betray themselves to be mixtures by the fact that different samples vary in their properties. Glass is such a material. It must be a mixture because it varies in its characteristics; yet, so far as we can tell, the particles that are intermingled are the individual molecules of calcium silicate and sodium silicate of which the glass is mainly composed.

Such a mixture of different kinds of molecules, as distinguished from one of different kinds of coarse particles, is a true solution. In dissolving a substance to form a solution, we get the same result as if we were to put it through a mill, capable of grinding it down to its very molecules. Such a process of subdividing one substance, and scattering its particles through another, is called **dispersion.** Thus, people who like to have science couched in very formal language are in the habit of defining solutions as **molecularly dispersed mixtures.**

Every solution must accordingly contain at least two different substances. One of these, commonly a liquid, is called the **solvent,** and is said to dissolve the other substance. The latter, that is to say, the substance dissolved, is called the **solute.** In many cases, however, it is impossible to draw such a distinction. In a solution containing roughly equal parts of water and alcohol, for example, either substance may be considered as the solvent. Each has, in fact, dissolved the other.

92. Importance of Solutions.—Many of the most interesting and important things in chemistry have to do with solutions. The air we breathe is a **gaseous solution.** The oceans are filled with a **liquid solution.** The oldest rocks of the earth's crust are **solid solutions,** while others were formed by crystallization from such solutions or from solution in water. Solutions carry mineral foods from the roots of plants to the topmost branches, and return with other materials, to be stored up as woody tissue, starch, or sugar, in stem, or leaves, or tubers. They carry out our digestive processes; they course through our veins; they form the fluid contents of every living cell. Thus, the whole aspect of our earth, and all the forms of life that exist upon its surface, are determined by the properties of solutions.

93. Complete and Partial Miscibility.—*Gases* may be dissolved in each other to form a gaseous solution, **in any desired proportion.** This is presumably because their molecules are relatively so far apart, and move with such slight interference that they intermingle freely. *Liquids* will mix in any desired proportion only when they are somewhat alike in their properties. This often means that they must be **chemically related**—having molecules built on similar architectural plans. Examples of such pairs of **completely miscible liquids** are water and alcohol, benzene and gasoline, lemon oil and turpentine. **Complete miscibility means that there is no limit to the solubility of one substance in the other.**

Liquids that are not so similar in their properties, or so closely related chemically, often cease to be completely miscible as soon as they have been cooled below a certain temperature. Thus, water and phenol (carbolic acid), from high temperatures down to 68° C., will dissolve in each other in any desired proportion; but below 68° they are but **partially miscible**—there is a limit to the solubility of each substance in the other. If we take a very large excess of either substance, the other may still dissolve in it completely. As soon as the limit of solubility is passed, however, we obtain two layers of liquid: a lower one consisting largely of phenol, with some dissolved water; and an upper one of water, with some dissolved phenol.

Liquids that are very dissimilar in their properties—such as water and benzene—are usually very slightly soluble in each other; and if shaken together will immediately separate into two layers, even though heated.

94. True *versus* Colloidal Solutions.—If a soluble, *crystalline* substance, such as sugar or common salt, is placed in a beaker of water, the crystals grow smaller and smaller, and finally disappear, *but maintain their original shape to the very last.* This is evidence that the atoms on the surface of the crystal are being stripped away in a regular and systematic manner, layer after layer. There is reason for believing that the material thus removed from the surface is dispersed so finely by the action of the solvent that we reach at last the *simple molecules* characteristic of the gaseous state of matter. Sometimes even these may be disrupted (§ 101). In other words, **crystalline substances usually dissolve to form true solutions** (but see § 376).

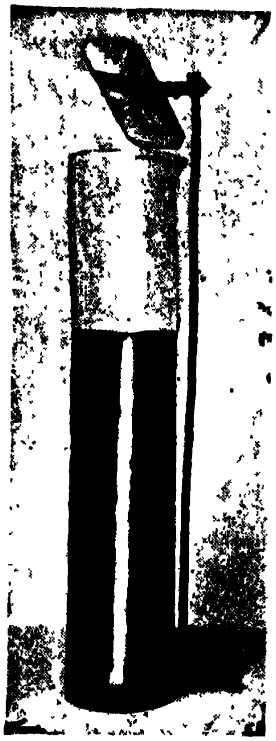

Fig. 35. — Tyndall test for colloidal particles.

On the other hand, if glue, a *non-crystalline* substance, is thrown into water, we observe quite the contrary effect. Instead of diminishing in size, as a crystal would do, the glue draws water into itself, and swells up enormously. In the end it may absorb forty or fifty times its own weight of water and still remain a fairly solid jelly. No wonder such a substance is said to be **hydrophilic** (Greek, *water-loving*). Although, in the end, the glue is dispersed through the water, evidence goes to show that it never reaches the state of extreme subdivision characteristic of the particles of salt or sugar dissolved in water, but persists as comparatively huge *groups of molecules.* Thus we have what is called a **colloidal solution,** in which the dispersed particles are of *intermediate size* between the simple molecules present in true solutions, and particles so large as to be visible with a microscope.

Colloidal solutions are often as clear and transparent as true solutions; but they may be recognized as colloidal solutions by the famous **Tyndall test,** shown in Fig. 35. If a beam of light is passed through the liquid, its path becomes beautifully illuminated, since each of the colloidal particles reflects a portion of the light toward the observer. A true solution, under similar circumstances, usually shows but a faint beam, due to dust particles. The tail of a comet is a gigantic Tyndall beam.

An **ultramicroscope** makes use of a beam of light rich in **ultraviolet light** – that is, light having a wave-length so short that it is invisible to human sight. This beam is passed into a few drops of the solution to be studied, in the field of a powerful microscope. With proper arrangements, particles too small to reflect ordinary light then appear as tiny scintillating sparks; for, in spite of their small size, they reflect and scatter a portion of the ultraviolet light, and in so doing increase its wave-length, so that it becomes ordinary light. Thus the ultramicroscope, with the aid of invisible light, makes colloidal particles visible.

ORDER OF INCREASING DEGREE OF DISPERSION OR DECREASING SIZE OF PARTICLES

Coarse suspensions	Very fine suspensions	Colloidal solutions	True solutions
Particles visible with naked eye.	Particles visible with microscope.	Particles may be visible with ultramicroscope.	Particles (simple molecules) far too small to be visible by any means.
Particles of diameter greater than $100\mu\mu$.*		Particles of diameter between 1 and $100\mu\mu$.	Particles of diameter less than $1\mu\mu$.

Colloidal solutions are of such great interest and importance that we shall devote an entire chapter to their consideration, at a later stage in our progress.

95. Saturated, Supersaturated, and Unsaturated Solutions.— If a solution contains as much of a dissolved substance as it **can continue to hold in the presence of undissolved crystals of the same**

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* The sign $\mu\mu$ (double *mu*) stands for the millimicron, or the one-millionth part of a millimeter.

substance, is it said to be **saturated.** Thus, if we place some crystals of common salt in water, shake or stir for several hours, and find that some of the crystals remain undissolved, we may be fairly sure that the solution we have formed is a saturated one.

A saturated solution in the presence of undissolved crystals is a case of *equilibrium* (§ 67)—here **molecular equilibrium.** Molecules dissolve from the surface of the crystal as fast as others of the same kind come out of the solution and are redeposited. That an exchange of this kind really takes place may be seen from the fact that a crystal with a broken corner, if hung in a saturated solution, will have the broken corner repaired at the expense of material taken from other parts of its surface.

Most substances dissolve more readily in hot water than in cold (§ 96). If a solution is saturated when hot, then filtered and cooled, it will often retain all of the material that it dissolved at the higher temperature, and will accordingly be more concentrated than one prepared directly by stirring crystals in cold water at the lower temperature. It is then said to be **supersaturated.**

Whether a solution is saturated, supersaturated, or unsaturated may be determined by noting what happens when an additional crystal of the given substance is thrown into it. If this dissolves, the solution is **unsaturated**; if it grows larger, the solution is supersaturated; if it remains of the same size, the solution is just saturated. Note that a saturated solution is not one that contains as much of the dissolved substance as it can be made to *dissolve*—but as much as it can be made to *retain*, in the presence of undissolved material of the same kind.

A **concentrated** solution is one that contains a relatively large *amount of solute in a given volume of solution. It may or may* not be fully saturated. A **dilute** solution is one containing a relatively small amount of solute and a relatively large amount of solvent.

96. Effect of Temperature on Solubility.—Most substances **increase in solubility with increasing temperature.** *Figure 36 illustrates* this fact in graphical form for a number of common salts. Thus, from the **solubility curve** of NH_4Cl, we see that a saturated *solution of this salt, at 20° C., contains 37 g. of dissolved salt in every 100 g. of water; but at 70° the solubility has increased to* 60g. in 100 g. of water.

Name the salts whose formulas are given in this chart. What weight of $K_2Cr_2O_7$ will separate if 100 g. of water, saturated with that salt at 90°, are allowed to cool to 20° C.? What weight of water will dissolve 100 g. of $KClO_3$, at 80° C.?

Gases, and a very few solids and liquids, become less soluble as the temperature is increased. Notice that sodium sulfate has two separate solubility curves: one for the anhydrous salt, Na_2SO_4; and one for the hydrated salt, $Na_2SO_4 \cdot 10H_2O$ (§ 80). Thus, at temperatures around 30°, sodium sulfate may have either one of two different solubilities, according to the type of crystal in equilibrium with the solution.

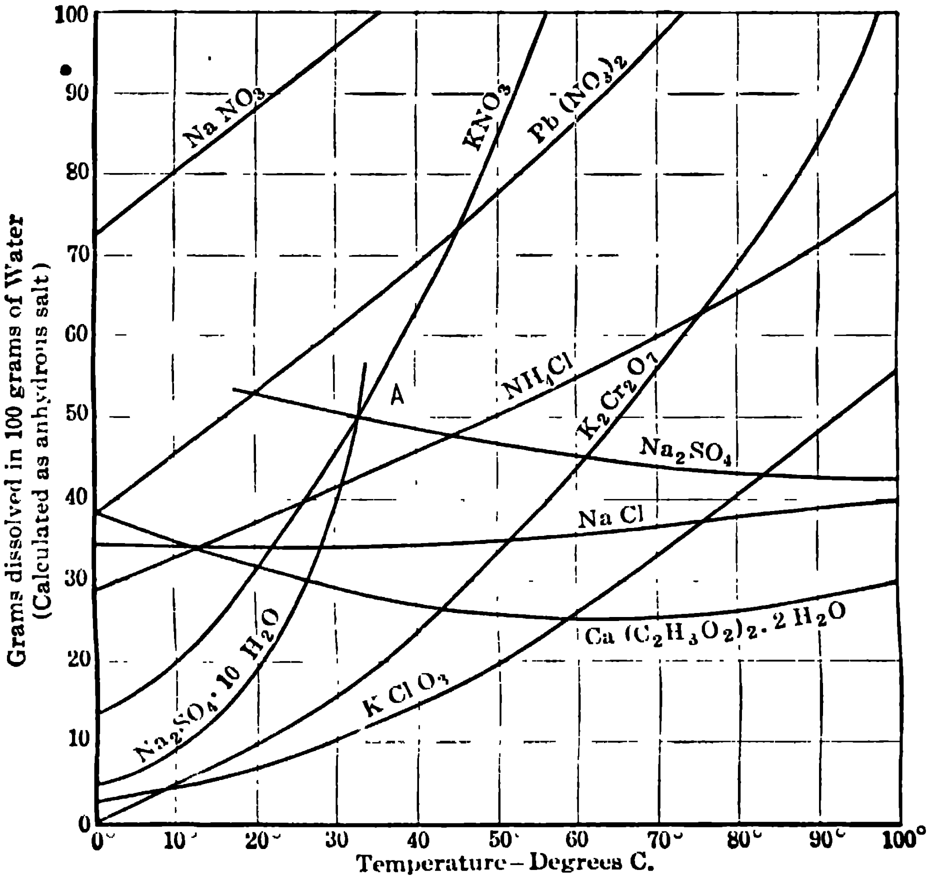

FIG. 36.—Solubility curves of a few common salts.

Which is the more soluble at 30°, the anhydrous or the hydrated salt?

Thus, in general, **the solubility of a given substance at a given temperature can be definitely stated only if we know which crystalline form of the substance is in equilibrium with the solution.**

97. Recrystallization.—The constituents of a mixture can often be separated by taking advantage of differences in their solubility. Thus, sea-water, from prehistoric times down to the present day, has been evaporated in artificial ponds, to prepare common salt. When the solution has become sufficiently concentrated, the salt begins to crystallize out, while the more soluble and less plentiful constituents of the solution mainly salts of calcium, magnesium, and potassium—remain behind in the **mother-liquor.**

Crystals obtained from a solution by a single crystallization are often far from pure, but may be purified by **recrystallization.** The more nearly alike the substances to be separated happen to be, in their solubility and chemical characteristics, the more recrystallizations will be necessary. In the purification of the rare earth salts, used in the manufacture of incandescent mantles (§ 593), and in the purification of radium salts (§ 586), hundreds of patient recrystallizations are often necessary.

98. The Law of Henry.—There is a great difference in the extent to which different gases dissolve in water. It is worth remembering that—

H_2, N_2, O_2	are but	**slightly soluble**	2 to 4 volumes in 100 of water;
CO_2, Cl_2, H_2S	are	**fairly soluble**	several hundred volumes in 100 of water;
SO_2, NH_3, HCl	are	**very soluble**	several thousand volumes in 100 of water.

These figures are for the solubility of the gases **at room temperature, under one atmosphere of pressure.** Their solubility **decreases with increasing temperature.**

If a gas is only *fairly soluble*, the weight dissolved in any given volume of liquid is *proportional to the pressure* (*Law of Henry*). But note that **the solubility of extremely soluble gases,** such as ammonia and hydrogen chloride, **does not increase so rapidly with increasing pressure as the Law of Henry would predict.**

The increased solubility of gases with increased pressure is used in the manufacture of carbonated drinks. When the stopper of a bottle of soda-water is drawn, the pressure is relieved and a part of the dissolved gas escapes, producing the familiar sparkling (*effervescence*). Workmen employed in compressed air chambers (caissons), used for tunneling under rivers, often fall down in convulsions on emerging into the open air, from the effect of air-bubbles which the release of pressure liberates from solution in the spinal fluid. The risk is diminished if a mixture of oxygen and helium is substituted for air (which is a mixture of oxygen and nitrogen); for helium is much less soluble than nitrogen. A very gradual release of the pressure affords the same protection.

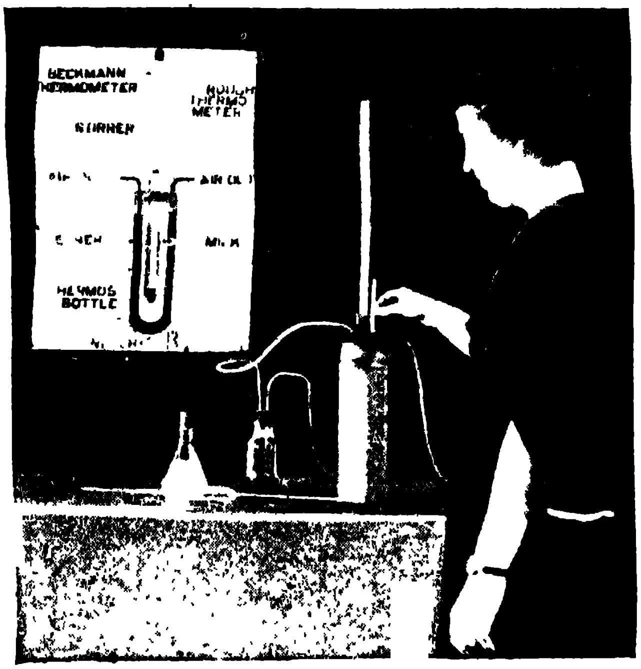

Fig. 37.—Testing milk for added water by a determination of its freezing point. Milk freezes at a temperature a trifle lower than water, because it is a solution; but the addition of a little water raises its freezing point. See *Jour. Ind. Eng. Chem.* 13, 202 (1921).

99. Freezing and Boiling Points of Solutions.—An important fact is that **solutions tend more strongly to remain in the liquid state than do the pure solvents from which they are formed.** This means **decreased tendency to evaporate or solidify.** Decreased tendency to evaporate implies that a solution has a **lower vapor pressure,** and consequently a **higher boiling point,** than the corresponding pure solvent; decreased tendency to solidify means that it has a **lower freezing point** (§ 99).

Illustrations of this general principle are seen on every hand: Honey—a solution of invert sugar and other substances in water—

has a lower vapor pressure than pure water, and may be exposed to the air indefinitely without evaporating, in situations in which pure water would soon disappear. The candy-maker, in boiling down a strong sugar syrup, must reach a much higher temperature than would be needed to boil pure water. Sea-water remains unfrozen when fresh-water lakes are covered with ice.

100. Osmosis. The facts just considered may be expressed by saying that **the tendency of the molecules of a solvent to escape from the liquid state is always decreased by dissolving any other substance in it.**

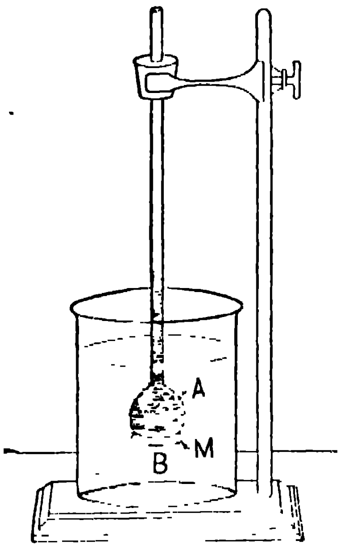

FIG. 38.—Osmosis.

This general principle may be illustrated in still another way (Fig. 38). A solution, say of cane-sugar in water, is placed in an inverted thistle-tube, *A*, separated by a suitable membrane, *M*, from pure water in a beaker, *B*. The membrane tends to absorb water both from the solution in *A* and from the pure water in *B*. But, of these two processes, the former takes place the more readily, for the water molecules from the solution find much the same difficulty in escaping into the membrane that they would find in evaporating or separating as ice.

Thus, when the membrane finally becomes saturated with water, with respect to the pure solvent in *B*, it is *supersaturated* with respect to the solution in *A*. The result is that some of the water acquired from the pure solvent is yielded up to the solution. Thus, molecules of water, from *B*, are transferred continuously into the membrane, passed through this by diffusion, and handed on to the solution in *A*. As a result, the solution in the liquid in the thistle-tube rises at the rate of perhaps an inch an hour, for a considerable length of time.

This movement of a solvent through a membrane into a more concentrated solution on the other side of the membrane is called *osmosis*.

If a solution is separated by a suitable membrane from the pure solvent, the pressure that needs to be applied to stop the transfer of solvent molecules through the membrane is called **osmotic pressure.** It has been measured with elaborate apparatus, and for many substances (in *dilute* solutions) has been found to be proportional to the **number of moles of solute contained in a given weight of solvent.** Thus one mole of cane sugar, $C_{12}H_{22}O_{11}$, dissolved in 1000 g. of water, produces a solution having very nearly the same osmotic pressure as one containing one mole of ethyl alcohol, C_2H_5OH, in 1000 g. of water.

What actual weights of sugar and of ethyl alcohol are represented by one mole of each? If *equal* weights of these two substances were dissolved in a given weight of water, which solution would have the higher osmotic pressure?

What weight of glycerol, $C_3H_5(OH)_3$, needs to be dissolved in a given weight of water to produce a solution having the same osmotic pressure as one containing one-tenth mole of cane sugar?

101. Ions.—Every acid, base, or salt consists of two parts—(1) a *metal* or *hydrogen*; (2) a *non-metal* or *non-metallic radical* (§ 71). These two parts often act quite independently of each other when the given substance is dissolved in water. This is fortunate, for chemistry is thereby enormously simplified. Thus, we do not need to specify which barium salt and which sulfate are needed to produce barium sulfate; for solutions of *all soluble barium salts* react with solutions of *all soluble sulfates* to form that familiar white precipitate:

$$\begin{array}{lcll} \textit{Barium Salts} & & \textit{Soluble Sulfates} & \\ \left.\begin{array}{l} BaCl_2 \\ Ba(NO_3)_2 \\ Ba(C_2H_3O_2)_2 \\ Ba(ClO_3)_2 \end{array}\right\} & \begin{array}{c}\text{reacting}\\ \text{with}\end{array} & \left\{\begin{array}{l} Na_2SO_4 \\ K_2SO_4 \\ MgSO_4 \\ Al_2(SO_4)_3 \end{array}\right\}, & \begin{array}{c}\text{all}\\ \text{produce}\end{array} \quad BaSO_4 \end{array}$$

We get the same product, barium sulfate, no matter what non-metallic radical is contained in the barium salt, and no matter what metal in the soluble sulfate. The **Ba** and the SO_4 combine to form $BaSO_4$, which precipitates. The other part of the barium salt and the other part of the soluble sulfate have not the least influence on the result.

Again, whenever an acid is mixed with a base, the two react to produce water:

$$\begin{array}{lcll} \textit{Acids} & & \textit{Bases} & \\ \left.\begin{array}{l} HNO_3 \\ HCl \\ HC_2H_3O_2 \\ H_2SO_4 \\ H_3PO_4 \end{array}\right\} & \begin{array}{c}\text{reacting}\\ \text{with}\end{array} & \left\{\begin{array}{l} NaOH \\ KOH \\ Ca(OH)_2 \\ Mg(OH)_2 \\ Fe(OH)_3 \end{array}\right\}, & \begin{array}{c}\text{all}\\ \text{produce}\end{array} \quad H_2O. \end{array}$$

The **H** of the acid and the **OH** of the base combine to form **H_2O**, no matter what the other part of the acid or base may be.

These facts show that the two parts of each acid, base, or salt are so readily separated from each other as to act quite independently in most reactions. This is really putting the case too mildly; for, if we pass a current of electricity through a solution of such a substance, the metallic part (or hydrogen) moves off in one direction and the non-metallic part in the opposite direction, as if the two parts were given the capacity for independent motion by the mere act of dissolving them in water. The fact that they move in opposite directions, under the influence of the electric current, shows them to carry electrical charges of opposite kinds.

Thus, we may conclude that **whenever acids, bases, or salts are dissolved in water, at least a part of their molecules are present as electrically charged fragments of molecules.** We call these fragments **ions,** and we say that the dissolved acid, base, or salt is partially or completely **ionized** or **dissociated.** Note that not all substances are ionized when dissolved in water. With a few exceptions, only acids, bases, and salts can be ionized and only when dissolved in water (and a few other solvents). Note, furthermore, that since ions have independence of action, constant chemical composition, and definite properties, they may be regarded as **substances** (§ 9). We shall speak of the properties of hydrogen-ion, a substance present in a solution of any acid in water; and of those of chloride-ion, a substance present in an aqueous solution of hydrochloric acid, or of any chloride salt. Note that **the electrical charge on an ion is the symbol of previous chemical change.** Thus, Na^+ is not metallic sodium, but sodium that has reacted with something else, to form sodium hydroxide or a sodium salt.

The names, symbols, and electrical charges of a few common ions should be committed to memory:

When dissolved in water, all

Acids	furnish	hydrogen-ion, H^+
Sodium salts	furnish	sodium-ion, Na^+
Potassium salts	furnish	potassium-ion, K^+
Silver salts	furnish	silver-ion, Ag^+
Barium salts	furnish	barium-ion, Ba^{++}
Ferrous salts	furnish	ferrous-ion, Fe^{++}
Ferric salts	furnish	ferric-ion, Fe^{+++}

Bases	furnish	hydroxyl-ion, OH^-
Chlorides	furnish	chloride-ion, Cl^-
Nitrates	furnish	nitrate-ion, NO_3^-
Acetates	furnish	acetate ion, $C_2H_3O_2^-$
Sulfates	furnish	sulfate-ion, SO_4^{--}
Phosphates	furnish	phosphate-ion, PO_4^{---}

Accordingly, we have two ways of speaking about chemical reagents. Very often, we can either say, "*any barium salt*," or else simply "*barium-ion*." Very often we can say "*any acid*," or else, "*hydrogen-ion*;" "*any base*," or else "*hydroxyl-ion*"; "*any chloride* (including HCl)", or else "*chloride-ion*." Some chemists habitually use one way of speaking, and some the other.

EXERCISES

1. Explain why glass is considered a solid solution. How may solid solutions be distinguished from true solids?

2. What reasons are there for calling air a solution? Is it properly described as a "a material" or a "substance"? Why?

3. Name several pairs of liquids that are completely miscible at ordinary temperatures, and several that are not.

4. From the solubility curve of ammonium chloride, determine how many grams of that salt dissolve in 100 g. of water at 50° C. How many grams of ammonium chloride is this for every 100 g. of solution?

5. Fresh fruits or vegetables, when first placed in strong brine often lose so much water that they are perceptibly shriveled. This is called *plasmolysis*. Is it related to osmosis, and if so how?

6. Compare the freezing and boiling points of solutions with those of pure water.

7. What is osmotic pressure? Describe an experiment to illustrate. What is the osmotic pressure of pure water?

8. What is the distinction between true and colloidal solutions? By what optical test may a colloidal solution usually be recognized?

9. Honey, or a fruit jelly, will often separate large quantities of sugar crystals, even though protected, to prevent evaporation. Explain.

10. A liter of water will dissolve about 4 cc. of oxygen, under one atmosphere of pressure. Under a pressure of 10 atmospheres, at 0° C., it will dissolve about 4 cc. of compressed oxygen. Show that this statement is in harmony with the Law of Henry.

11. What volume of water is needed to dissolve 1 kg. of ammonium chloride, at 50° C.? If the solution occupies 2400 cc., what is its specific gravity (§ 173)?

12. Explain the fact that the solubility curve of sodium sulfate consists of two sections, which intersect.

13. If 3 mg. of nitrogen dissolve in 1 liter of water at a certain temperature, under a pressure of 1140 mm. of mercury, how much will dissolve at the same temperature in 50 cc. of water, under a pressure of 15 atmospheres?

14. What weight of acetone, $(CH_3)_2CO$ must be dissolved to produce a solution having the same osmotic pressure as one containing 23 g. of ethyl alcohol, C_2H_5OH, in any given amount of water?

15. What classes of substances are partially or completely ionized, and under what circumstances?

16. Which of the following substances are ionizable? Which are not, and why? Hydrochloric acid; metallic zinc; barium chloride; solid, insoluble ferric hydroxide.

17. Explain why Fe is regarded as a different substance from Fe^{++} or Fe^{+++}.

18. Precipitation is regarded as the direct union of ions to produce molecules of an insoluble substance. Write an equation for the precipitation of the insoluble base, ferric hydroxide.

19. Reword the following sentences (see last paragraph of § 101) to indicate the ions concerned:

(*a*) A precipitate is formed whenever a solution of any silver salt is added to a solution containing hydrochloric acid or any metallic chloride.

(*b*) When an acid reacts with a base, one product is always water.

(*c*) Ferric hydroxide is an insoluble substance, produced by interaction of any ferric salt with any base.

(*d*) Ferrous salts produce ferric salts, on being oxidized.

CHAPTER VIII

ACIDS, BASES, AND SALTS

102. Acids.—The most important properties of acids are the following:

1. Acids cause certain substances, called **indicators,** to change color. For example, all but the least active acids turn blue litmus red.

2. Solutions of all acids of reasonable activity taste sour. (One needs to make sure that they are sufficiently diluted with water to be safe to taste.)

3. Acids react with the most active **metals** to form hydrogen gas and salts:

$$2HCl + Zn = \underset{\substack{\text{Zinc}\\\text{chloride}\\\text{(a salt)}}}{ZnCl_2} + H_2\uparrow.$$

The metal is here said to **displace** hydrogen from the acid.

4. Acids react with **bases** to form salts and water:

$$H_2SO_4 + \underset{\substack{\text{Zinc}\\\text{hydroxide}\\\text{(a base)}}}{Zn(OH)_2} = \underset{\substack{\text{Zinc}\\\text{sulfate}\\\text{(a salt)}}}{ZnSO_4} + H_2O.$$

The formula of the salt is like that of the acid except that the metal takes the place of hydrogen. The metal is therefore said to **replace** the hydrogen.

5. Acids hasten (**catalyze,** § 52) certain reactions in which water is one of the reactants. Thus, if a small amount of any active acid (as HCl, HNO_3, H_2SO_4) is added to a solution of ethyl acetate, the fragrant odor of the latter, after a few hours or days, gives place to the sharp odor of acetic acid (vinegar):

$$\underset{\substack{\text{Ethyl}\\\text{acetate}}}{C_2H_5(C_2H_3O_2)} + H_2O = \underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} + \underset{\substack{\text{Acetic}\\\text{acid}}}{HC_2H_3O_2}.$$

The acid that is added serves merely as a catalyzer.

All acids are composed of hydrogen, in combination with a non-metal or non-metallic radical (often called an electro-negative radical). Examples, HCl, H_2SO_4, H_3PO_4. But whenever the acid is dissolved in water, the two parts of the acid act independently, in many reactions. This fact, and others, indicate that at **least a part of the acid molecules are present in the water solution, as electrically charged fragments of molecules, called ions** (§ 101). The acid is then said to be partly dissociated. (**Dissociation** is a process of decomposition in which the resultants have the capacity for recombining, to give back the original substance.)

The five properties listed above, which all acids have in common, and which distinguish acids from other substances, are assumed to be the properties of the only ion that is common to all acids, namely hydrogen-ion, H^+. Accordingly, there are two different ways of defining an acid: (1) by stating the chief **properties** common to all acids, as given above; or (2) by stating that **an acid is a substance that dissociates in such a way as to furnish hydrogen-ion, when dissolved in water.** The former of these two definitions is at first the more practically useful; but the latter is perhaps the more precise, and should become the more suggestive at later stages of our study.

Compare with the definition of the word "acid," in a good dictionary.

103. Active and Inactive Acids.—If we wish to make a fair comparison of the properties of two different acids, we must dilute them until equal volumes contain the same amount of **acid hydrogen.*** We then that they are of **equivalent concentration.** Thus, a solution containing one mole of HCl has the same amount of acid hydrogen as one containing one mole of $HC_2H_3O_2$, or one-half mole of H_2SO_4, or one-third mole of H_3PO_4. If these solutions are diluted until they occupy equal volumes, they will be of equivalent concentration. They will then react with equal weights of any given metal, and with equal weights of any given base, and their properties may accordingly be fairly compared.

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* By acid hydrogen is meant all the hydrogen displaceable by metals, in the acid itself (as distinguished from the water). In acetic acid, $HC_2H_3O_2$, note that only the one atom first written in the formula is displaceable by metals. The other three are combined with other atoms in such a way that they cannot thus be displaced. They form part of the "acetate radical."

1. What actual weights of these four acids are here indicated? What weight of acid hydrogen is contained in the given weight of acid, in each case?

2. How many grams of acetic acid must be dissolved in a liter of water to furnish a solution of equivalent concentration to one containing 3.645 g. of hydrochloric acid in a liter?

If we make up dilute solutions of different acids, all of equivalent concentration—and it makes little difference how dilute they are, so long as we keep them equivalent—we discover that **different acids differ greatly in the degree to which they display acid properties.** Thus, a solution of hydrochloric acid (1) reddens litmus much more readily, (2) tastes much more sour, (3) reacts more *rapidly* with metals, (4) reacts more *completely* with bases, and (5) makes a much better catalyzer (for reactions catalyzed by acids) than a solution of acetic acid, of equivalent concentration. We express this by saying that hydrochloric acid is an **active** acid, and that acetic acid is comparatively **inactive.**

Now, the five properties that are characteristic of acids (which furnish five *tests* by which the activity of acids may be compared), are assumed to be the properties of **hydrogen-ion, H^+.** Accordingly, **the active acids owe their activity to the circumstance that nearly all their molecules, when dissolved in water, are dissociated into ions.** They are said to be "largely ionized," or "almost completely dissociated." Thus, with hydrochloric acid, the dissociation may be formulated:

$$HCl \rightleftarrows H^+ + Cl^-.$$

The double arrow here indicates that the dissociation is a reversible reaction, and is thus somewhat incomplete (§ 67). We have used a full-line arrow from left to right, but only a dotted arrow from right to left, to show that the former reaction predominates. In other words, when hydrochloric acid is dissolved in water, the equilibrium is such that most of it, at any one moment, exists as ions, H^+ and Cl^-, rather than as molecules, HCl. Of course, if we could observe a cinematograph record of events within a droplet of solution, we should doubtless observe that hydrogen ions,* H^+, were combining with chloride ions, Cl^-, to form molecules of HCl; but that other molecules of HCl were dissociating into ions, at the same rate. Thus, the fractional part of all the acid existing as ions would remain constant.

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* Note that we write hydrogen-ion (with a hyphen) when we speak of the particular *substance* that is present in solutions of all acids; but hydrogen ions (without the hyphen) when we are speaking of the electrically charged *particles* that make up that substance. Similarly for other ions.

Since acetic acid, on the other hand, is but slightly active, we assume that it is but "slightly ionized." By this we mean that relatively little of it, at any one moment, exists as ions, H^+ and $C_2H_3O_2^-$; but most of it as molecules, $HC_2H_3O_2$. Thus the dissociation may be formulated:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- .$$

We have here used a dotted arrow from left to right, and a full-line arrow from right to left, to show that the latter *reaction* predominates.

When slightly active acids are very much diluted, a somewhat larger proportion of their molecules are dissociated into ions. We shall discuss this later (§ 258).

3. Write equations to represent the fact that nitric acid is very active, while hydrofluoric acid (HF) is very slightly active
4. Cranberry juice may taste more sour than strawberry juice, even though both may be capable of reacting with the same quantity of soda. Explain.

The following table, giving the names, formulas and relative activities of a few common acids, should be committed to memory.

	Active Acids	*Moderately Active Acids*	*Slightly Active Acids**
These are **solutions** of gases, having the formulas given. In the gaseous form, when perfectly dry, they do not have the properties of acids.	HCl Hydrochloric acid		HF Hydrofluor acid
	HBr Hydrobromic		HCN Hydrocyani acid
	HI Hydriodic acid		H_2S Hydrosulfur acid †

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* The very slightly active acids are sometimes classified as *inactive*, though no acid could be completely inactive without ceasing to be an acid.

† More commonly called hydrogen sulfide.

	Active Acids	*Moderately Active Acids*	*Slightly Active Acids*
These are **hypothetical acids.** By this we mean that they have not themselves been prepared. We assume their existence from the fact that solutions of CO_2, SO_2, and N_2O_3 have the properties of acids, and form salts containing the radicals here indicated.		H_2SO_3 Sulfurous acid	HNO_2 Nitrous acid H_2CO_3 Carbonic acid
These are **liquids,** when pure	HNO_3 Nitric acid H_2SO_4 Sulfuric acid	H_3PO_4 Phosphoric acid	$HC_2H_3O_2$ Acetic acid
These are **solids** (commonly carrying water of hydration, § 79, not shown in these formulas.		$H_2C_2O_4$ Oxalic acid	H_3BO_3 Boric acid

5. What prefix do the preceding names have, when the acids contain no oxygen?

6. Compare the formulas for nitric and nitrous and for sulfuric and sulfurous acids. What relative amount of oxygen does the ending *-ous* seem to indicate, as compared with the ending *-ic*?

104. Preparation of Acids from Non-metallic Oxides.— Acids containing oxygen may usually be prepared **by direct union of a non-metallic oxide** (otherwise called an **acid-forming oxide**) **with water.** (§ 58.)

Sulfur dioxide gas combines with water to form *sulfurous* acid:

$$SO_2 + H_2O = H_2SO_3.$$

Sulfur trioxide (a white solid) combines with water to form *sulfuric* acid:

$$SO_3 + H_2O = H_2SO_4.$$

Phosphorus pentoxide (a white solid) combines with water to form *metaphosphoric* acid:

$$P_2O_5 + H_2O = 2HPO_3.$$

Non-metallic oxides which are capable of combining with water to form acids are called **acid anhydrides.**

7. Write and balance equations for the formation of nitric acid from nitrogen pentoxide, N_2O_5; nitrous acid from nitrogen trioxide, N_2O_3; and arsenious acid, H_3AsO_3, from arsenic trioxide, As_2O_3. What is the formula of sulfuric acid anhydride?

105. Preparation of Volatile Acids.– Substances that are **volatile** are those that can be vaporized at comparatively low temperatures (§ 10). Among the acids, these include the gases (HCl, HBr, HI, HCN) and the liquids of low boiling-point (HNO_3, $HC_2H_3O_2$). Comparatively **non-volatile** are the liquids H_2SO_4 and H_3PO_4.

Volatile acids are most readily prepared by treating their salts with a less volatile acid (usually H_2SO_4 or H_3PO_4).

Thus we obtain *hydrogen chloride*, HCl, often called *hydrochloric acid gas*, by treating one of its salts, such as sodium chloride, with sulfuric acid:

$$NaCl + H_2SO_4 = \underset{\text{Sodium acid sulfate}}{NaHSO_4} + HCl\uparrow$$

The sulfuric acid is poured through a thistle-tube (*T*, Fig. 39), over crystals of sodium chloride, in a flask. On warming the flask, the hydrogen chloride is expelled as a colorless gas with a suffocating odor. It produces heavy clouds of white fumes when it comes in contact with the moist air of the room, and is so very soluble that it cannot be collected over water, as are oxygen and hydrogen. It is much heavier than the air, however, and may be passed through a glass tube to the bottom of a bottle, as shown in the sketch, like so much water, air being displaced upward as the gas enters. If we dissolve some of the gas in water, the solution has a sour taste, reddens blue litmus, reacts with zinc, etc. It is hydrochloric acid. When all the sodium chloride originally present in the flask has been transformed, the reaction is complete. The flask then contains a salt called sodium acid sulfate, $NaHSO_4$, together with an unchanged excess of sulfuric acid.

8. What is meant when we say that we have used an excess of sulfuric acid?

9. Explain (§ 68) why the given reaction becomes complete.

Nitric acid is commonly prepared by heating sodium nitrate in a *retort* (Fig. 40) with concentrated sulfuric acid. Below about 86° C. the reaction is incomplete; but above that temperature the nitric acid distills off as fast as formed. Thus, again, we have a complete reaction:

$$H_2SO_4 + NaNO_3 = NaHSO_4 + HNO_3 \uparrow .$$

10. Write equations showing the preparation of acetic acid and hydrofluoric acid from their sodium salts.

We may usually use any other salt of the volatile acid we are to prepare instead of the sodium salt. Instead of sulfuric acid, we may employ phosphoric acid. In case the acid used as a reagent in preparing the volatile acid is itself volatile, a mixture of both acids distills over into the receiver. Furthermore, care must be taken that the acid we use does not react with the one we are to produce (§ 301*c*).

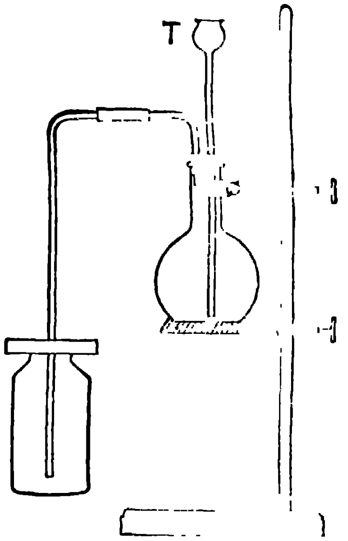

Fig. 39. Preparation of hydrogen chloride.

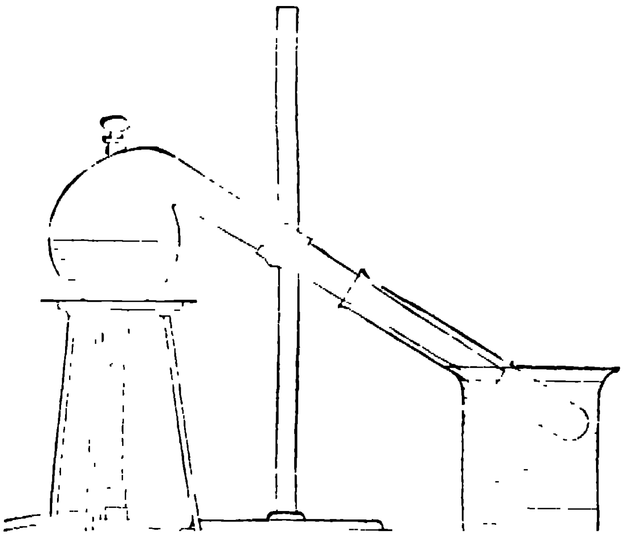

Fig. 40.—Preparation of nitric acid.

11. What is obtained in the receiver when sodium acetate is distilled with an excess of hydrochloric acid?

12. Write and balance an equation for the preparation of nitric acid from calcium nitrate, $Ca(NO_3)_2$, using phosphoric acid, the other product being calcium acid phosphate, $CaHPO_4$.

106. Bases.—The substances called bases are in sharp contrast with acids:

1. Bases cause indicators to change to a different color from that shown in the presence of acids. Thus, all but the least active bases turn red litmus blue.

2. Solutions of the most active bases (the **alkalies**) feel soapy, and have a bitter (alkaline) taste. (One needs to make sure that they are sufficiently diluted with water to be safe to taste.) Example, a dilute solution of sodium hydroxide, $NaOH$ (also called lye or caustic soda).

3. Bases react with acids to form salts and water:

$$\underset{\substack{\text{Sodium}\\\text{hydroxide}\\\text{(a base)}}}{NaOH}+HCl=\underset{\substack{\text{Sodium}\\\text{chloride}\\\text{(a salt)}}}{NaCl}+H_2O.$$

Most of the important bases are **metallic hydroxides** * (that is, substances composed of a metal in combination with the hydroxyl radical, OH). Examples:

$NaOH$	KOH	$Ca(OH)_2$	$Fe(OH)_3$
Sodium hydroxide	Potassium hydroxide	Calcium hydroxide	Ferric hydroxide

But in ammonium hydroxide, NH_4OH (and in some less important bases) a group of non-metallic atoms (here the ammonium group, NH_4) plays the part of a metal. Such a group is called an **electro-positive radical.**

The properties just given, which all bases have in common, are assumed to be the properties of **hydroxyl-ion,** OH^-, since this is the only ion that is common to solutions of all bases of whatever kind. Thus, a base may be defined (1) by stating the chief **properties** common to all bases; or (2) by stating that **a base is any substance that dissociates in such a way as to furnish hydroxyl-ion, when dissolved in water.**

Compare with the definition of the word "base," in a good dictionary.

107. Active and Inactive Bases.—Bases, like acids, differ enormously in the degree to which they display their characteristic properties. To make a fair comparison, we must prepare solutions of equivalent concentration, that is, solutions in which equal volumes are capable of reacting with equal weights of some given acid. We then find that the group of extremely soluble bases called **alkalies**—LiOH, NaOH, KOH,—(1) affect indicators more readily, (2) taste more distinctly alkaline, and (3) react more *completely* with acids than other bases do. We express this by saying that the alkalies are extremely **active** bases. We explain their activity by assuming that they are very largely dissociated into ions, in dilute solution;

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* An older view, which still lingers in many books dealing with the industrial applications of chemistry, regards the corresponding metallic *oxides* (Na_2O, K_2O, CaO, Fe_2O_3) as bases. It is better to call them base-forming oxides, or basic oxides

$$NaOH \rightleftarrows Na^+ + OH^-.$$

Thus, at any given moment, most of any dissolved sample of sodium hydroxide exists as ions, Na^+ and OH^-, rather than as molecules, NaOH.

Ammonium hydroxide, by all these tests, proves to be comparatively **inactive.** We assume that it is very incompletely dissociated into ions, in dilute solution:

$$NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

At any given moment, very little of any dissolved sample of ammonium hydroxide exists as ions, NH_4^+ and OH^-.

Memorize the following:

Active Bases	*Somewhat Less Active Bases*	*Slightly Active Bases*
LiOH	$Ca(OH)_2$	NH_4OH
NaOH	$Sr(OH)_2$	$Mg(OH)_2$
KOH	$Ba(OH)_2$	$Al(OH)_3$
		Hydroxides of the heavy metals *

13. Name the bases listed here. Write ionic equations to express the fact that aluminum hydroxide is much less active than calcium hydroxide.

108. Preparation of Bases.—The three chief methods for preparing bases are:

1. By direct union of metallic oxides with water:

$$CaO + H_2O = \underset{\text{Calcium hydroxide}}{Ca(OH)_2}.$$

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* Such as iron, copper, lead, and other metals occupying the middle portion of the *Periodic Table*, printed on the back cover of this text.

This is the process of "slaking lime," familiar to everyone who has seen plaster prepared (§ 456).

2. By action of active metals on water:

$$Mg+2H_2O=\underset{\text{Magnesium hydroxide}}{Mg(OH)_2}+H_2\uparrow.$$

This is one of our general methods for preparing hydrogen (§ 66).

14. Explain which metals (§ 72) are sufficiently active to decompose water.

15. How many moles of water are needed to produce one mole of magnesium hydroxide? What actual weight of water is this for each mole of magnesium hydroxide? What actual weight of water for each gram of magnesium hydroxide?

16. Write and balance equations for the action of potassium, calcium, and aluminum on water (formulas in § 107).

3. By action of other bases on salts. If the reaction is to be complete, a precipitate or a slightly active base must be formed.

(*a*) Precipitate is an **insoluble base** (hydroxide of magnesium or a heavy metal):

$$MgSO_4+2NaOH=Na_2SO_4+Mg(OH)_2\downarrow.$$

$$FeCl_3+3NH_4OH=3NH_4Cl+Fe(OH)_3\downarrow.$$

(*b*) Precipitate is an **insoluble salt:**

$$Na_2CO_3+Ca(OH)_2=2NaOH+CaCO_3\downarrow.$$

This is a method by which sodium hydroxide has been prepared (§ 435) for thousands of years, for the manufacture of soap.

(*c*) **A slightly active base** is formed:

$$NH_4Cl+NaOH=NaCl+\underset{\text{A slightly active base}}{NH_4OH}.$$

This reaction is of practical advantage whenever we wish to make a faintly alkaline solution still less alkaline. We merely add any ammonium salt.

Solutions of ammonium hydroxide are generally prepared by dissolving ammonia gas, NH_3, in water.

17. Write equation. Why is ammonium hydroxide called a hypothetical base (§ 103)?

109. Salts.—Review (§ 101). Whenever an acid acts on a metal or a base, one of the products is a salt. A salt is thus a substance that is derived from an acid when the hydrogen of the acid is **displaced** by a metal, or **replaced** by the metallic part of a base.

Most salts are crystalline solids, which may or may not contain water of hydration (§ 79). **Salts containing Cr, Mn, Fe, Co, Ni, Cu, are usually colored.** Salts containing only the other common elements are usually white. (Find these six metals in the Periodic Table, printed on the back cover.)

18. Give the formulas of the following salts, met in preceding work: Sodium sulfate, sodium acid sulfate, sodium nitrate, sodium acetate, copper sulfate, barium sulfate, zinc chloride.

All salts are composed of metals or electro-positive radicals, in combination with non-metals or electro-negative radicals. Otherwise expressed, all salts, when dissolved in water, dissociate in such a way as to furnish two kinds of ions: (1) metallic (**electro-positive**) ions—including ammonium ion, NH_4^+; and (2) non-metallic (**electro-negative**) ions. Salts, unlike acids and bases, have no general properties, since no one ion is common to all of them. Thus, solutions of certain salts taste salty, others bitter, sour, or "metallic." (Many salts are dangerously poisonous.) Solutions of salts also vary in their action on indicators, some turn blue litmus red, others turn red litmus blue, while many have no action. Finally, salts vary enormously in their solubility in water. One gram of water will dissolve almost 5 g. of zinc chloride but only about a millionth of a gram of silver chloride, at room temperature.

19. Explain why electro-positive and electro-negative ions are so called. Give examples

20. Draw up a definition for the word salt, based on the ions that salts can furnish, but worded in such a way as to exclude acids and bases. Compare with the definition given in the dictionary.

Evidence goes to show that salts (with very few exceptions) are almost completely dissociated when dissolved in water.

21. Write equations expressing this fact for NaCl and for Na_2SO_4.

110. Acid, Basic, and Normal Salts.—When an acid is treated with a limited quantity of a base, it often happens that only part of the hydrogen of the acid is replaced by the metal contained in the base. Thus, when sulfuric acid is treated with a limited quantity of sodium hydroxide, only one of the two hydrogen atoms in the molecule of sulfuric acid is replaced by sodium. The product, $NaHSO_4$, is an acid salt.

$$H_2SO_4 + NaOH = \underset{\substack{\text{Sodium acid}\\ \text{sulfate}}}{NaHSO_4} + H_2O.$$

If an excess of sodium hydroxide is used, both hydrogen atoms are replaced by sodium, and we get a **normal salt,** Na_2SO_4.

22. Write and balance equation.

23. Write and balance three equations for the action of sodium hydroxide on phosphoric acid, in such a way that one, two, and three atoms of hydrogen, respectively, in each molecule of the acid, are replaced by sodium.

Acid salts, therefore, are those formed when *only a part* of the hydrogen of an acid is replaced by a metal. They share the properties of acids in that they still contain **hydrogen replaceable by metals.** But note that acid salts do not necessarily react acid toward litmus. They do so only when the acid from which they are derived is at least moderately active.

24. Which of the following acid salts will probably react acid toward litmus, and why? $NaHSO_4$, $NaHCO_3$, $NaHSO_3$, $NaHF_2$.

Conversely, when a base is treated with a limited quantity of an acid, it sometimes happens that only a part of the hydroxyl groups of the base are replaced by the non-metal or electro-negative radical contained in the acid. Thus, zinc hydroxide, when treated with a limited quantity of hydrochloric acid, forms basic zinc chloride.

$$Zn(OH)_2 + HCl = \underset{\substack{\text{Basic zinc}\\ \text{chloride}}}{Zn(OH)Cl} + H_2O.$$

Basic salts are accordingly salts containing hydroxyl or oxygen * that is replaceable by non-metals or non-metallic radicals. Other examples are basic ferric acetate, $Fe(OH)_2C_2H_3O_2$, and basic lead carbonate $Pb(OH)_2 \cdot 2PbCO_3$ (an important paint pigment, called "white lead," § 580). It is a common practice to write the formulas of basic salts in this way, as if they were combinations of a metallic hydroxide or oxide with a normal salt. Basic salts rarely react alkaline toward litmus.

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* A salt containing oxygen, rather than hydroxyl, replaceable by non-metals, would be called an *oxy-salt* by some chemists. Actually, no such distinction should be made. For basic salts, like most bases, contain an indefinite quantity of water (§ 471), and are thus only very inaccurately represented by the formulas commonly assigned to them. As this water is removed they pass over imperceptibly into the so-called oxy-salts.

A **normal salt** is one containing neither hydrogen replaceable by metals nor hydroxyl (or oxygen) replaceable by non-metals.

Examples: KCl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $Mg_3(PO_4)_2$. Solutions of normal salts vary in their action on indicators (§ 113).

25. Name these salts. Name, and give the formula of, the acid and base from which each is derived. Which of these acids is the least active? Which of these bases?

111. Solubility of Salts.—Reactions in which *soluble* substances interact to produce *insoluble* ones have two great practical advantages. (1) They are always complete (§ 68). (2) The insoluble product (a precipitate) may always be separated from other products, merely by filtration. Accordingly, many of the operations of Analytical Chemistry and many important applications of chemistry to industry make use of reactions of this type. A simple **Table of Solubilities** is worth committing to memory:

1. Sodium, potassium and ammonium salts are *soluble* (with rare exceptions, § 444).

2. Nitrates and acetates are *soluble* (except a few basic nitrates and acetates).

3. The following salts, among many others * are *very slightly soluble*:

(*a*)	$AgCl$ Silver chloride	$HgCl$ Mercurous chloride	$PbCl_2$ Lead chloride
(*b*)	$PbSO_4$ Lead sulfate	$CaSO_4$ Calcium sulfate	$BaSO_4$ Barium sulfate

(*c*) All carbonates and phosphates, except those of sodium and potassium. Examples:

$CuCO_3$ Copper carbonate	$MgCO_3$ Magnesium carbonate	$MnCO_3$ Manganese carbonate

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* A more complete list of insoluble salts, given in § 426, is best studied at the beginning of a course in Qualitative Analysis.

(*d*) Sulfides and hydroxides of all the heavy* metals. Examples:

CuS	Ag_2S	FeS
Copper sulfide (black)	Silver sulfide (brown)	Ferrous sulfide (dark brown)

26. From the general statement in § 109, determine which of these insoluble salts are white, and which colored, and make penciled notes in the table above.

27. Explain the meaning of the single and double stars in the Table of Solubilities that faces the back cover of this text. (See printed matter, below the table.)

28. What figure is there given for the solubility of lead chloride, in moles per liter?

29. How many grams of barium sulfate will dissolve in 100 liters of water?

112. Preparation of Salts. —Of the many different methods for preparing salts (§ 427) we shall here mention six:

1. **Metal and non-metal.** Metals unite directly with non-metals, to form salts. Thus, powdered iron, when heated with powdered sulfur, combines with the sulfur to form a brittle, dark-brown solid, ferrous sulfide.

$$Fe+S=FeS.$$

2. **Metal and acid.** Active metals will react with non-oxidizing acids to form a salt and hydrogen. (Review § 72.)

30. Name two oxidizing and two non-oxidizing acids. Which of these will react with zinc? Which with copper? In which cases will hydrogen be evolved, and in which some gas other than hydrogen?

3. **Metal and salt.** Metals react with the salts of other metals, less active than themselves, in such a way as **to displace the less active metal.** Iron is more active than copper (§ 72). Thus, a sheet of iron, placed in a solution of copper sulfate, soon becomes covered with a bright coating of metallic copper. Some of the iron has reacted, displacing copper from the copper salt:

$$Fe+CuSO_4=\underset{\text{Ferrous sulfate}}{FeSO_4}+Cu.$$

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* The heavy metals are iron, copper, lead, and other metals whose symbols appear in the middle portion of the *Periodic Table*, on the back cover of this book.

31. What actual weight of iron is needed to prepare one gram-atom of copper by this method? What weight of iron for one gram of copper?

32. Name three other metals which are more active than copper, and which therefore displace copper from a solution containing any copper salt.

33. Explain why solutions of zinc salts may be kept in copper tanks, while solutions of silver salts may not.

4. **Base or metallic oxide and acid.** A reaction between a base and an acid, to produce a salt and water, is called **neutralization.** Since the distinctive properties of both acid and base disappear as a result of the reaction, each is said to **neutralize** the other. If a normal salt is formed, the neutralization is said to be complete; otherwise it is incomplete.

34. Write and balance an equation for the complete neutralization of sulfuric acid by sodium hydroxide. How many moles of sodium hydroxide are needed for each mole of sulfuric acid?

35. If one mole of sodium hydroxide is used for each mole of sulfuric acid, what salt is formed?

Sometimes the term neutralization is extended to include the interaction between an acid and a *carbonate*, to form a salt, water, and carbon dioxide. (This illustrates Method 5, which follows.) Thus, the housewife may neutralize the acid of sour milk (lactic acid) by soda (sodium carbonate); and the farmer may neutralize acid soils by applying finely ground limestone (calcium carbonate).

36. Write and balance an equation for the complete neutralization of acetic acid by sodium carbonate. How many moles of acetic acid are needed for each mole of carbon dioxide gas liberated?

5. **Salt and acid.** A salt may react with an acid to form another salt and another acid. If such a reaction is to be practically useful, it must be complete. This means that the acid to be produced must be *volatile* or *slightly active*.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3 \uparrow .$$

We were formerly interested in this reaction as a means of preparing a *volatile acid*, nitric acid (§ 105). Now we see that it is also a useful means for preparing a salt; for when the acid is distilled away, sodium acid sulfate remains behind in the receiver.

Another example, in which the completeness of the reaction is due to the *slight activity* of one of the products, is

$$NH_4C_2H_3O_2 + \underset{\text{An active acid}}{HCl} = NH_4Cl + \underset{\text{A slightly active acid}}{HC_2H_3O_2}.$$

This reaction is of practical advantage whenever we wish to make a faintly acid solution still less acid. We merely add any salt of any slightly active acid (for example, any acetate.)

6. **Salt and salt.** Two salts may react together to form two other salts. If the reaction is to be complete, however, one of the two salts formed must be **insoluble.** It will then separate as a precipitate (§ 68);

$$CaCl_2+Na_2CO_3=2NaCl+CaCO_3\downarrow.$$

Note that in this reaction the calcium and the sodium exchange places. The calcium, originally combined with chlorine, goes into combination with the carbonate radical; and the sodium, originally combined with the carbonate radical, goes into combination with chlorine. Reactions of this type, in which a metal exchanges places with another metal (or with hydrogen) are cases of **double decomposition.** The term is in common use, but is somewhat misleading, for the process is really one of double replacement—each metal replaces the other.

37. Write an equation for a reaction of neutralization, and show that neutralization is a special case of double decomposition.

Sometimes double decomposition is of use when one of the two products is not insoluble, but merely *less soluble* than the other. Thus, when sodium nitrate and potassium chloride are mixed, a double decompostion takes place, resulting in two *soluble* salts.

$$NaNO_3+KCl \rightleftarrows KNO_3+NaCl.$$

The reaction is therefore incomplete; but one of the two products, NaCl, is much less soluble than the other, and crystallizes out first if the solution is evaporated. If these crystals are removed by filtration, the remaining mother liquor can be made to yield KNO_3, which may be purified by recrystallization (§ 97). (For the details of such a process, consult a laboratory manual.) The incomplete double decomposition thus becomes of some practical use, after all.

38. From the following list of soluble substances, select eight pairs of substances that react to produce a precipitate when their solutions are mixed. Name the *precipitate* in each case. Name the *soluble substance* produced in each case. Silver nitrate, barium chloride, sodium phosphate, zinc sulfate, ammonium sulfide, calcium hydroxide, and potassium carbonate.

39. The "chrome yellow" of street cars and yellow cabs is an insoluble salt, lead chromate. Name two soluble salts which should react to produce "chrome yellow," when their solutions are mixed.

The ionic interpretation of these six methods of forming salts, (§ 138), may be introduced next, if desired.

113. Hydrolysis.—Review the last item of § 88. Many substances react with water in such a way as to produce two new substances, one of which contains *hydrogen*, the other *hydroxyl*, derived from the water. Such reactions are cases of **hydrolysis.** For example, when phosphorus trichloride is poured into water, there is a violent reaction:

$$\underset{\text{Phosphorus trichloride}}{PCl_3}+3HOH=\underset{\text{Phorphorous acid}}{P(OH)_3}+3HCl.$$

The original phosphorus trichloride is here completely hydrolyzed. One of the two reaction products, phosphorous acid, contains hydroxyl, derived from the water; while the other reaction product, hydrochloric acid, contains hydrogen, derived from the water.

Hydrolysis is of great importance in the applications of chemistry. Thus, cotton or linen cloth is generally treated, before dyeing, with a chromium, aluminum, iron, or copper salt (called a **mordant**). By hydrolysis, a basic salt or metallic hydroxide is formed, and is precipitated upon and within the fibers:

$$\underset{\text{Chromium acetate}}{Cr(C_2H_3O_2)_3}+2HOH=\underset{\text{Basic chrom acetate}}{Cr(OH)_2C_2H_3O_2}+2HC_2H_3O_2.$$

Goods thus treated are dyed more readily than untreated cotton or linen, and the dye taken up is less readily washed out; for the basic salt clings firmly to the fiber, and the dye, in turn, to the basic salt. Something similar happens when chromium salts are employed in tanning leather.

Again, many baking powders owe their action to the fact that they contain hydrolyzable salts (such as alum). The acid set free by hydrolysis acts on the other ingredient of the baking powder (sodium acid carbonate), releasing carbon dioxide gas, which causes the dough to rise:

$$NaHCO_3+H_2SO_4 = NaHSO_4+H_2O+CO_2\uparrow.$$

Finally, most of the ingredients of our food are hydrolyzed during the process of digestion. Thus they are converted into substances of simpler chemical composition, which find their way through the intestinal walls into the blood stream, and there are built up again into living tissue.

In the special case in which *salts* are hydrolyzed, we may regard hydrolysis as the reverse of neutralization:

$$\underset{\text{Base}}{Fe(OH)_3} + \underset{\text{Acid}}{3HCl} \underset{\text{Hydrolysis}}{\overset{\text{Neutralization}}{\rightleftarrows}} \underset{\text{Salt}}{FeCl_3} + \underset{\text{Water}}{3HOH}.$$

Not all salts are hydrolyzed by water, however. In any particular case, recall whether the acid and base from which the salt is derived by neutralization are active or inactive. **A salt derived from an active base and an active acid is not noticeably hydrolyzed.** If either the base or the acid is slightly active, the salt will be *partly* hydrolyzed. If both acid and base are slightly active, the salt will always be *very largely* hydrolyzed. For example, common salt, NaCl, which is derived from an active base (NaOH) and an active acid (HCl) is not hydrolyzed by water. (Think what might happen to marine life if the case were different.) Zinc sulfate, derived from a slightly active base and an active acid, is partly hydrolyzed. Aluminum carbonate, derived from a slightly active base and a slightly active acid, is almost completely hydrolyzed.

40. Write an equation for the hydrolysis of zinc sulfate, in such a way as to show that the hydrolysis is incomplete.

41. Is sodium fluoride, NaF, slightly or almost completely hydrolyzed, and why?

42. Name two salts that should not be appreciably hydrolyzed by water; two that should be partly hydrolyzed; two that should be very largely hydrolyzed.

(The ionic explanation of hydrolysis, §§ 267–269, may be introduced here, if desired.)

114. Action of Salt Solutions on Indicators.—What we have just said concerning the hydrolysis of salts gives us a clue to the action of solutions of different salts on indicators. **Solutions of normal salts affect indicators only when these salts are somewhat hydrolyzed**—for the reason, of course, that normal salts contain no replaceable H or OH, and therefore cannot furnish hydrogen-ion or hydroxyl-ion except as a result of interaction with water. There are four cases to consider.

1. Normal salts derived from *active acids* and *active bases*. No appreciable hydrolysis, and the salt solutions therefore neutral.

2. Normal salts derived from *active acids* and *slightly active* bases. Slight hydrolysis, producing equivalent amounts of acid and base:

$$CuSO_4+2HOH \rightleftarrows Cu(OH)_2+H_2SO_4.$$

But the acid thus produced is more active than the base. Accordingly, though acid and base are present in equivalent total concentration (§ 103), more hydrogen ions will be present in the solution than hydroxyl ions, and the solution will react somewhat acid toward sufficiently sensitive indicators. Actually, the base from which the salt is derived must be less active than ammonium hydroxide, if the solution is to affect litmus—turn blue litmus red.

3. Normal salts derived from *slightly active acids* and *active bases*. Slight hydrolysis, resulting in equivalent amounts of acid and base:

$$Na_2CO_3+2HOH \rightleftarrows 2NaOH+H_2CO_3.$$

But the base thus produced is more active than the acid; hence more hydroxyl ions will be present than hydrogen ions, and the solution will react alkaline toward sufficiently sensitive indicators. Actually, the acid concerned must be less active than acetic acid, if the solution is to affect litmus—turn red litmus blue.

4. Normal salts derived from *slightly active acids* and *slightly active bases*. Considerable hydrolysis. The resulting solution will be neutral or faintly acid or alkaline, according to the relative activities of acid and base.

The preceding discussion relates to the reaction of solutions of normal salts. Acid salts react acid toward litmus if the acid from which they are derived is of moderate activity; otherwise they may react neutral or alkaline, as a result of hydrolysis. Soluble basic salts react basic if derived from a base of reasonable activity; otherwise they may react neutral or acid, as a result of hydrolysis.

43. What will be the reaction of solutions of the following salts toward litmus, and why? Ammonium acetate, sodium sulfate, potassium carbonate, zinc chloride, ferric nitrate, potassium cyanide (derived from HCN), ammonium sulfide (derived from H_2S), and calcium acetate.

44. Tell how one may determine, from the reaction of the sodium salt of an acid, whether the acid itself is active or slightly active.

45. Tell how one may determine, from the reaction of a chloride salt, whether the base from which the salt is derived is active or slightly active.

115. Titration.—Whenever a definite weight of one substance reacts with (or is prepared from) a definite weight of another, the two weights are said to be **chemically equivalent.** If to a given weight of one substance, *A*, we add more than the chemically equivalent amount of another substance, *B*, we are said to have employed an **excess of** *B*. This may happen even though the weight of *B* is less than that of *A*. Thus 2 moles (= 80 g.) of sodium hydroxide are chemically equivalent to 1 mole (= 98 g.) of sulfuric acid, in the reaction:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Then, if we should use 85 g. of sodium hydroxide with 98 g. of sulfuric acid, there would be an excess of sodium hydroxide, of about 5 g.

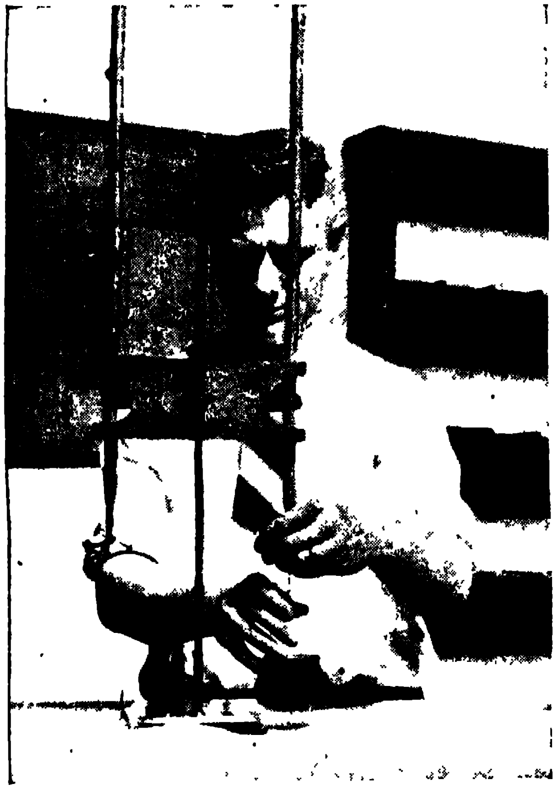

Fig. 41.—Titrating a base with an acid.

46. What weight of sodium sulfate is chemically equivalent to 80 g. of sodium hydroxide?

47. What weight of oxygen is chemically equivalent to 1.008 g. of hydrogen?

Very often, substances that are to enter into a reaction are brought together as solutions of known concentration, i.e., a definite number of grams of each substance in a cubic centimeter of solution. To determine what weights of the two substances are chemically equivalent to each other, we then need only note the volumes of the solutions used.

In one experiment, 25 cc. of an alkaline solution, known to contain 0.040 g.

of sodium hydroxide in each cubic centimeter, were carefully measured out and discharged into a beaker; then a few drops of an indicator solution were added. On adding a dilute sulfuric acid solution from a buret (Fig. 41), 26.40 cc. were needed for neutralization.

This acid solution was known to contain 0.0464 g. of sulfuric acid in each cubic centimeter. Thus, altogether, there were used $25 \times 0.040 = 1.000$ g. of sodium hydroxide and $26.40 \times 0.0464 = 1.225$ g. of sulfuric acid These weights of acid and base are therefore chemically equivalent.

An experiment in which the volumes of reacting solutions are measured and compared is called a **titration.**

Normal solutions, §§ 148–151, may be introduced next, if desired.

116. Salts in Industry.—Many salts are found in practically inexhaustible deposits, in nature. Four of them are the basis of some of the world's greatest industries, which involve investments of billions of dollars.

Salts	*Substances Prepared from these Salts*	*Uses of These Substances*
NaCl (Common salt)	NaOH (Caustic soda)	Soap, rayon (artificial silk), paper, metallic sodium, sodium peroxide; purifying petroleum and vegetable oils.
	Na_2CO_3 (soda)	Glass, water-glass; softening water; neutralizing acids.
	Na_2SO_4 (Sodium sulfate)	Glass, textiles, paper.
	Cl_2 (Chlorine)	Bleaching; disinfectants, dyestuffs, chloroform and many other organic chlorine compounds; purifying drinking water.
	HCl (Hydrochloric acid)	Cleaning metal surfaces; purifying bone-black for refining of sugar. Dyestuff industry.
$CaCO_3$ (Limestone)		Limestone itself is used for building stone, Portland cement, and preparation of iron, zinc, and copper from their ores; and to neutralize acidity, in agriculture and other industries.

Salts	*Substances Prepared from these Salts*	*Uses of These Substances*
$CaCO_3$	CaO (Quicklime)	Plaster; manufacture of soda, leather, paper, sugar, glass, bleaching powder, caustic soda, carbonated drinks. Refrigeration; purifying coal-gas.
	CaC_2 (Calcium carbide)	Manufacture of acetylene, ammonia and other nitrogen compounds; fertilizers, acetic acid, solvents.
$CaSO_4 \cdot 2H_2O$ (Gypsum)		Plaster of Paris, stucco, wall-board, interior decorations, paper, Portland cement, paint, molds used in the manufacture of pottery and porcelain.
FeS_2 (Iron pyrite)	H_2SO_4	Preparation of most other acids; superphosphate fertilizer; storage cells for automobiles; purifying petroleum. See § 213.

117. Summary.—

	Constituents	*Ions Yielded*	*Characteristic Properties*	*Preparation*
Acids	Hydrogen + electro-negative radical	H^+ and electro-negative ion	Litmus turned red. Sour taste. React with metals. Neutralized by bases. Catalyzers for many reactions.	Non-metallic oxide + water. Salt of volatile acid + less volatile acid.
Bases	Metal + hydroxyl	Metallic ion and OH^-	Litmus turned blue. Bitter taste. Neutralized by acids.	Metal + water. Metallic oxide + water. Salt + another base.
Salts	Metal + electro-negative radical	Metallic ion + electro-negative ion	No general properties. Hydrolysis § 113.	See § 112.

Commit to memory:

List of active and slightly active acids, § 103.
List of active and slightly active bases, § 107.
Colors of salts, § 109.
Rules concerning solubility, § 111.
Methods for preparing salts, § 112.
Reactions of solutions of normal salts toward litmus, § 114.

EXERCISES

1–47. Review the preceding questions of this chapter.

48. Name three plant juices that contain noteworthy quantities of acid. Is the sour taste of these juices an indication of the total amount of base that a given volume of juice can neutralize? Why, or why not (§ 273)?

49. Describe the inversion of cane sugar (§ 371) and tell how the process might be used to compare the activity of two different acids.

50. A solution of potassium chlorate is neutral toward litmus. One of potassium hypochlorite is strongly alkaline. What conclusion may be drawn, and why, concerning the relative activities of the two acids from which these salts are derived?

51. Draw up formal definitions of the following terms, then quote the most nearly corresponding definitions given in the dictionary: Neutralization, hydrolysis, dissociation, indicator, titration, ion, volatile.

52. When are two acid solutions said to be of equivalent concentration?

53. When is a basic solution of equivalent concentration to an acid solution?

54. Write and balance an equation for the complete neutralization of sulfuric acid by sodium hydroxide. What weight of sulfuric acid must be dissolved in a liter of water to prepare a solution of equivalent concentration to one containing one mole of sodium hydroxide in a liter?

55. Mention five tests by which the activity of two acids may be compared directly. Mention another test, dependent on the reactions of solutions of their sodium salts toward indicators.

56. Write an equation for the neutralization of a base by a slightly active acid. Use this equation to explain the relationship of neutralization to hydrolysis.

57. Which salts are largely hydrolyzed by water, which slightly hydrolyzed, and which are not hydrolyzed at all? Give examples of each class.

58. Which of the salts listed in question 43 (§ 114) are neutral toward litmus, but would probably be found to be alkaline or acid toward indicators more sensitive to H^+ or OH^-?

59. Are H^+ and OH^- properly referred to as substances? Why, or why not?

60. What are the characteristic properties of hydrogen-ion? Of hydroxyl-ion?

61. When are the names of ions hyphenated, and when not? Illustrate.

62. Tell how sodium hydroxide is most readily prepared from sodium carbonate.

63. Restate the last two sentences in § 108 in terms of ions. (See last paragraph of § 101.)

64. Tell how each of the following acids may be prepared: Acetic acid, phosphoric acid, nitric acid, sulfurous acid, hydrochloric acid. Write equations.

65. Tell how each of the following bases may be prepared: Sodium hydroxide, calcium hydroxide, magnesium hydroxide (3 ways).

66. Which of the six methods that have been discussed for the preparation of salts will apply to each of the following: Sodium chloride, magnesium sulfate, potassium acetate, lead chloride. Write equations.

CHAPTER IX

VALENCE AND FORMULAS

118. How to Derive the Formulas of Salts from those of Acids and Bases.—Whenever an acid neutralizes a base, each H atom from the acid combines with one OH group from the base, to form HOH. Accordingly, the number of H atoms (and ions) furnished by the acid must be *equal* to the number of OH radicals (and ions) furnished by the base. The metallic part of the base and the non-metallic part of the acid then remain in the solution as ions of the corresponding salt.

This gives us a method by which the formulas of salts may be derived. For example, let us derive the formula of *magnesium phosphate*:

1. Recall the formulas of the base (§ 107) and the acid (§ 103) from which the salt is derived by neutralization.

$$Mg(OH)_2 \qquad\qquad H_3PO_4$$

2. Note how many molecules of base and of acid must be taken to obtain equal numbers of OH and H.

In the given case, 3 molecules of base and 2 of acid will furnish 6OH and 6H. The solution will then contain 3 Mg^{++} ions and 2 PO^{---} ions.

3. Write the formula of the salt by assuming that the metallic ions and non-metallic ions then remaining combine with each other (as they would do if the solution were evaporated until the salt crystallized out).

$3Mg^{++}$ combines with $2PO_4^{---}$ to form $Mg_3(PO_4)_2$.

As another example, note that aluminum sulfate is derived from $Al(OH)_3$ and H_2SO_4. To get equal numbers of OH and H, we must take $2Al(OH)_3$ and $3H_2SO_4$. We then have left $2Al^{+++}$ ions, which combine with 3 SO_4^{--} ions, to form $Al_2(SO_4)_3$.

1. Check the following formulas, by the method just outlined:

Aluminum acetate, $Al(C_2H_3O_2)_3$
Calcium chloride, $CaCl_2$
Aluminum phosphate, $AlPO_4$
Magnesium nitrate, $Mg(NO_3)_2$
Ammonium carbonate, $(NH_4)_2CO_3$
Sodium sulfate, Na_2SO_4
Ammonium oxalate, $(NH_4)_2C_2O_4$
Barium sulfate, $BaSO_4$
Potassium nitrate, KNO_3
Calcium acetate, $Ca(C_2H_3O_2)_2$

119. Valence.—The method we have just outlined enables us to derive the formulas of hundreds of salts, as soon as we have committed to memory the formulas of a very few acids and bases. We can apply the process a little more easily, however, if we make use of **valence**—that property of any atom or group of atoms that determines how many atoms or radicals of other kinds combine with it. The valence of any metal (as it exists in a given base or in any salt derived from that base) is measured by **the number of hydroxyl radicals with which one atom of the metal combines in forming the base.** Thus, the valence of sodium (in $NaOH$ and all sodium salts) is +1; the valence of magnesium (in $Mg(OH)_2$ and all magnesium salts) is +2; and that of aluminum (in $Al(OH)_3$ and all aluminum salts) is +3. (The valence of metals is considered positive, since they form positively charged ions when bases and salts are dissolved in water.)

Conversely, the valence of any non-metal or non-metallic radical (as it exists in a given acid or in any salt derived from that acid) is measured by **the number of atoms of hydrogen with which one atom of the non-metal (or one non-metallic radical) combines in forming the acid.** Thus, the valence of Cl (in HCl and all chlorides) is −1; that of SO_4 (in H_2SO_4 and all sulfates) is −2; that of PO_4 (in H_3PO_4 and all phosphates) is −3. (The valence of non-metals and non-metallic radicals is considered negative, since they form negatively charged ions when acids and salts are dissolved in water.) We may note now that **the number of charges on any ion** (Mg^{++}, Cl^-, SO_4^{--}, PO_4^{---}) **is the number indicated by its valence.**

2. What is the valence of each element or radical in the ten compounds whose formulas are listed at the close of the preceding section?

3. What is the valence of H and OH in HOH? (Consider water, for the moment as being either a base or an acid.) What is the valence of O in H_2O?

4. Turn to the list of formulas of ions, in § 101, and verify the fact that the charge carried by each agrees with its valence.

120. The Rule of Valence.—Note that the word valence applies to *individual* atoms and radicals. Thus, when we say that the valence of aluminum, in $Al_2(SO_4)_3$, is $+3$, we mean that *each* of the 2 aluminum atoms may combine with 3 hydroxyl groups. We may, nevertheless, speak of the 2 aluminum atoms as possessing altogether $+6$ **units of valence.**

The rule we have developed (§ 118) for deriving the formulas of salts then comes to this: Write the formula of every salt in such a way that the units of positive valence are *equal* to the units of negative valence. Otherwise expressed, **in every formula the algebraic sum of all the units of valence** (positive and negative) **is zero.** This is sometimes called the **Rule of Valence.** It will permit us to write the formulas of many other substances than acids, bases, and salts, if we assume that oxygen, in such compounds, has a constant valence of -2, and hydrogen a constant valence of $+1$. Note that we use the *least possible* number of atoms or radicals that will satisfy the Rule of Valence, unless we have experimental evidence that some multiple of the simplest formula represents the actual composition of a molecule. Thus we write $MgSO_4$, not $Mg_2(SO_4)_2$; and $Al(NO_3)_3$, not $Al_2(NO_3)_6$.

5. Check the ten formulas at the close of the preceding section, by the Rule of Valence.

6. Assuming that the metals concerned have their customary valence, and oxygen a valence of -2, write the formulas of the oxides of sodium, magnesium, and aluminum.

7. What must be the valence of sulfur in H_2SO_4, in order that the Rule of Valence may be satisfied?

8. What must be the valence of nitrogen in NH_4Cl, in order that the Rule of Valence may be satisfied? Of nitrogen in HNO_3?

121. The Valence of Elements within Radicals.—Two examples (7 and 8) have just been given to show that the Rule of Valence may be used to determine the valence of individual elements within radicals. The valence of each element is always what it needs to be in order that the algebraic sum of all the units of valence in the given molecule may be zero.* For example, in potassium dichromate, $K_2Cr_2O_7$, the two potassium atoms together possess +2 units of valence, and the seven oxygen atoms −14 units of valence. Thus the two chromium atoms together must possess +12 units, in order that the sum of all the units within the molecule may be zero. This is +6 units of valence for each chromium atom, hence, we say that the valence of chromium in potassium dichromate is +6.

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* This rule may result in a different valence for carbon than the valence (4) that organic chemists usually assign to that element. In any case it gives merely the *average valence*, when several atoms of a given kind have different valences. We may regard it merely as an arbitrary device which to be put to practical use in balancing equations involving oxidation and reduction (§ 135).

Note that chromium, in the most familiar chromium salts, has the valence of +3. In chromates and dichromates, however, it has the valence +6. This illustrates the fact that **metals sometimes enter into and form part of electro-negative ions** (e.g., the chromate ion, CrO_4^{--}; or the dichromate ion, $Cr_2O_7^{--}$). Under such circumstances, metals often possess a **higher valence** than they do when they form electro-positive ions of bases and salts.

9. Work out the valence of the element other than oxygen within the radical in KIO_3, K_3AsO_4, KOH, $KMnO_4$, K_2CrO_4, $Ca(NO_2)_2$, $HC_2H_3O_2$.

10. What is the valence of the radical itself in each of these substances?

11. Write equations (§ 103) to show the manner in which these six substances are dissociated when dissolved in water, being sure to give each ion a charge corresponding to its valence.

12. Give an example to illustrate the proposition that the sum of all the units of valence within a *radical* is equal to the valence of the radical as a whole.

122. The Valence of Metals.—Up to the present moment, the list of formulas of bases, which we committed to memory in § 107, has served to give us the valence of some common metals; but a more complete list is here tabulated on the following page. In each case, **the metal is assumed to be present as the electro-positive ion of a base or salt.**

Note that whenever a metal manifests two different common valences, the salts that it forms in the lower valence are distinguished by the ending **-ous**; and those that it forms in the higher valence by the ending **-ic**. Thus, stannous chloride (lower valence) is $SnCl_2$, and stannic chloride (higher valence) is $SnCl_4$. Ferrous sulfate (valence of iron, +2) is $FeSO_4$; and ferric sulfate (valence of iron, +3) is $Fe_2(SO_4)_3$.

Commit this table to memory:

Valence +1 (Univalent Metals)	*Valence +2 (Divalent Metals)*	*Valence +3 (Trivalent Metals)*	*Valence +4 (Quadrivalent Metals)*
Na	Mg	Al	
K	Ca	Cr	
NH_4	Sr	Bi	
Ag	Ba	Sb	
	Mn		
	Pb		
	Ni		
	Cu		
Hg (in mercurous salts)	Hg (in mercuric salts)		
	Fe (in ferrous salts)	Fe (in ferric salts)	
	Sn (in stannous salts)		Sn (in stannic salts)

13. Apply the Rule of Valence to determine the valence of the metal in each of the following formulas, then give the name of each substance:

HgF_2, HgF	SnO, SnO_2
$Fe(OH)_2$, $Fe(OH)_3$	Hg_2O, HgO
$Mn(C_2H_3O_2)_2$, $Mg(C_2H_3O_2)_2$	$FePO_4$, $Fe_3(PO_4)_2$

14. Write formulas of the following: Mercuric nitrate, mercurous nitrate, magnesium nitrate, ferrous oxalate, ferric acetate, stannous hydroxide, stannic oxide.

15. Compare the valence of manganese in $MnSO_4$ with its valence in $KMnO_4$; and the valence of lead in $Pb(C_2H_3O_2)_2$ and $Pb(OH)_2$ with its valence in Na_2PbO_3. Which statement in § 121 is illustrated by these formulas?

16. Give the name and formula (including the charge) of the electropositive ion furnished by:

All mercurous salts.	All mercuric salts.
All ferrous salts.	All ferric salts.
All stannous salts.	All stannic salts.

17. Write equations to show the ionization of ferrous acetate and ferric acetate, respectively, being sure to give each ion a charge corresponding to its valence.

123. How Valence is Indicated.— Valence is often indicated by small numerals placed above and to the right of the symbol of the element or group concerned. Thus, $H_2^{+1}S^{+6}O_4^{-2}$ indicates that the sulfur in sulfuric acid has a valence of +6 and that *each* of the four oxygen atoms has a valence of −2. (Occasionally, accents or Roman numerals are used, and algebraic signs disregarded: $H_2{}'S^{VI}O_4{}''$.)

Valence may also be indicated, in the case of ionizable substances, by giving the formulas of the ions that are furnished when the given substance is dissolved in water. For we have already noted that the charge on the ion is numerically equal to the valence of the corresponding element or radical. Thus, we may write $Al_2{}^{+++}(SO_4)_3{}^{--}$ to indicate that *each* of the two aluminum atoms has a valence of +3; and *each* of the three sulfate radicals a valence of −2. Some chemists prefer the one method of indicating valence, and some the other.

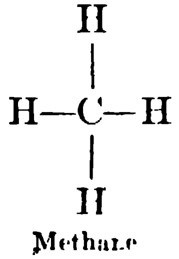
18. Mark the valence of the different metals and radicals in Problems 13 and 14, above.

19. Write the formulas of the following substances, in such a way as to indicate the valence of *each element*:

Potassium chlorate, phosphoric acid, potassium permanganate, mercurous sulfide (valence of sulfur, −2), mercuric nitrate.

124. Structural Formulas.—The valence of an element determines the number of atoms or radicals of other kinds that may combine with one atom of the given element. Now let us indulge in a flight of fancy, and picture the units of valence possessed by any given atom or radical as so many mechanical connectors, such as hooks, for connecting it with other atoms. Disregarding algebraical signs, an atom of carbon (valence, +4 or −4) would be pictured as possessing four hooks; an atom of oxygen (valence, −2) as possessing two hooks; and an atom of hydrogen (valence, +1) as possessing one hook.

Now let us hook atoms together in such a way as to leave no hooks uncombined. Then, representing each combination of a hook with a hook by a straight line (commonly called a **valence bond**), we have **structural formulas**, such as the following:

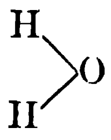


$$\begin{array}{c} H \\ | \\ H{-}C{-}H \\ | \\ H \end{array}$$

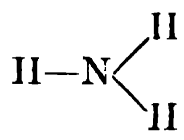
Methane

$O{=}C{=}O$

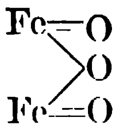
Carbon dioxide



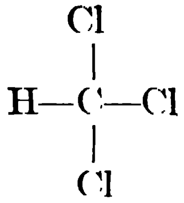
Water



Ammonia

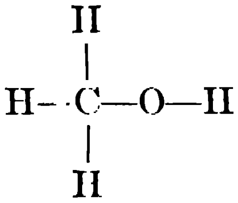


Ferric oxide



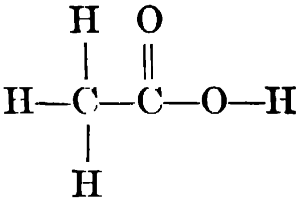
$$\begin{array}{ccc} & \text{Cl} & \\ & | & \\ \text{H}— & \text{C} & —\text{Cl} \\ & | & \\ & \text{Cl} & \end{array}$$

Chloroform



$$\begin{array}{ccc} & \text{H} & \\ & | & \\ \text{H}— & \text{C} & —\text{O}—\text{H} \\ & | & \\ & \text{H} & \end{array}$$

Methyl alcohol



$$\begin{array}{cccc} & \text{H} & \text{O} & \\ & | & \| & \\ \text{H}— & \text{C} & —\text{C} & —\text{O}—\text{H} \\ & | & & \\ & \text{H} & & \end{array}$$

Acetic acid

Note that the valence of each element (disregarding its sign) is given by the number of straight lines that proceed from the symbol of the element.

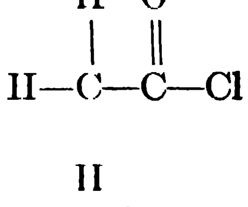
20. Show that the valence of C, O, and H in the formulas just given, is in every case that specified above.

21. Write a structural formula for formaldehyde, HCHO, that will give each element its proper valence.

Note, furthermore, that the straight lines that proceed from any given atom may be disposed in any convenient direction. Their *number* is the important thing.

22. Alter the formula of acetic acid, so that it presents an entirely different appearance from that shown above, without being different with regard to the valence or order of connection of the atoms concerned.

From all that has thus far been said, it might be imagined that structural formulas were the result of pure speculation. This is far from the truth. For when the idea of valence has been applied to show what sort of structural formulas are possible for any given molecule, experiments are at once devised to determine which of these represents the true order of connection of the atoms with each other. Thus, in the case of acetic acid, one of the four hydrogen atoms is known to be connected with oxygen, rather than with carbon; for when acetic acid is treated with any one of several different reagents, one fourth the hydrogen and half the oxygen step out *together*, and are replaced by chlorine. Thus we obtain:



$$\begin{array}{ccc} & \text{H} & \text{O} \\ & | & \| \\ \text{H}— & \text{C} & —\text{C}—\text{Cl} \\ & & \\ & \text{H} & \end{array}$$

Acetyl chloride

Structural formulas are "the architectural plans of molecules," in the sense that they show the relationship of the different parts of each given molecule to each other; but they are hardly to be considered as picturing the actual arrangement of atoms in space. They are very useful in that they help us to remember the **characteristic reactions** of the substances concerned. More important still, the unraveling of the structural formulas of useful substances is generally a necessary prelude to their **synthesis** from simple and cheap materials; for it is hardly possible for us to build a given molecule until we know the plan upon which it is constructed.

During the century in which chemists have been at work on the subject, the structural formulas of at least two hundred thousand compounds have been worked out. Those given here are among the simplest. In contrast, the structural formula of a dyestuff might occupy most of this page. Structural formulas find their chief use in dealing with organic compounds. Among inorganic compounds, they are apt to be misleading, in that they fail to show the important difference in the nature of the valence in ionizable substances, such as $SnCl_4$, as contrasted with that in non-ionizable substances such as CCl_4. Moreover, they are based on an arbitrary assumption, which makes the valence of oxygen, almost always, *two*. Very recently, structural formulas of a different kind have been proposed, based on our present knowledge of the cause of valence (§ 125). These, however, have not yet come into general use, and many books still present structural formulas for ionizable substances as if they were no different in their nature from non-ionizable ones.

23. Work out such a structural formula for sulfuric acid, assigning to sulfur a valence of $+6$.

125. Electrons, and what they Have to do with Valence.— Valence, by its very definition, is a property of the individual atoms of the elements or of groups of atoms (radicals) which act as individual atoms. Therefore, if we wish to explain why atoms differ in valence, we must digress for a glimpse of the manner in which atoms appear to be constructed. Our fanciful pictures of atoms being held together by something like hooks and eyes were well enough as a means of introducing the idea of structural formulas, but, after all, what does hold atoms together?

The first clue comes from the observation that all solids, when first suitably purified, and then heated in a vacuum, emit negative electricity. Thus it appears that negative electricity is a constituent of all atoms, of whatever kind. Furthermore, some very beautiful experiments * on the discharge of electricity through rarefied gases † have shown that negative electricity is no more continuous than is matter, but exists as small, equal, individual charges, called **electrons.** These electrons are the ultimate units of which any given charge of negative electricity is composed. An electric current, flowing through a wire, appears to be simply a stream of electrons, handed on from atom to atom, along the path of the current. Some idea of the extremely small quantity of electricity represented by a single electron may be had from the statement that 36×10^{18} ‡ electrons stream through the filaments of a pair of automobile headlights, drawing 6 amperes of current, during each second that the current passes.

The presumption then, is that all atoms contain electrons. Some experiments, which cannot be described here, make it seem probable that many of these are in the outer portion of the atom, at a considerable distance from a central portion, which carries an equivalent amount of positive electricity. Thus the atom as a whole is electrically neutral. It is known that metallic atoms part with their electrons more readily than non-metallic atoms. This is presumably the reason why metals tend to form positively charged ions. These are simply metallic atoms which have *lost* one or more electrons, and which therefore have a surplus of positive electricity, corresponding to their valence. Thus, Al^{+++} represents an atom of aluminum which has lost three electrons. Negatively charged ions, on the other hand, are simply atoms or groups of atoms that have *gained* one or more electrons from some outside source. Thus, SO_4^{--} represents a group that has gained two electrons.

When a molecule of sodium chloride is ionized,

$$NaCl \rightleftarrows Na^{+} + Cl^{-},$$

---

* See books on the Structure of Atoms, *Appendix K.*

† A rarefied gas is one that is confined under a very low pressure, so that there are relatively few gas molecules in any given volume.

‡ Namely, 36, followed by eighteen zeros—thirty-six million million million.

we think of the process as one in which the molecule is decomposed, in such a way that the Na carries with it one *less* electron, and the Cl one *more* electron, than atoms of these elements normally possess. Thus the sort of valence that is represented by electrical charges carried by ions—so-called **polar valence**—is due to the *transfer* of one or more electrons, from an atom or group of atoms that tends to part with electrons, to an atom or group of atoms that tends to acquire them. The two oppositely charged ions tend to hold each other together by electrical attraction; but in some instances this attraction is so very much weakened by the presence of the solvent (water) that the substance concerned is almost completely dissociated into its ions.

The other sort of valence, represented by the union between atoms of a non-ionizable substance, or by the union between atoms within a radical – so-called **non-polar valence** – is believed to be due to electrons that do not belong completely to either of the two neighboring atoms, but are *shared* between them, in such a way as to hold the two atoms together. The union between neighboring carbon atoms, in most organic compounds, is an example of non-polar valence.

In either case, then, **atoms are held together by electrical forces, which are determined by the arrangement of electrons in the outer portions of atoms.**

24. What two kinds of ions are furnished when calcium nitrate, $Ca(NO_3)_2$, ionizes? What transfers of electrons take place during this ionization?

25. Turn to the list of electrons in § 101, and explain the charges that they carry, in terms of electrons.

126. How Salts are Named.

—(This section may be postponed, if desired, to be included in review, somewhat later in the course.)

Acids and their salts may be divided into **five groups**, according to the relative amounts of oxygen they contain.

I. Hydrochloric Group.

Certain acids have names beginning with the **prefix *hydro-*** and ending with the **termination *-ic*.** This signifies that they contain **no oxygen.** The following are important:

Hydrofluoric acid,	HF	Hydrocyanic acid,	HCN
Hydrochloric acid	HCl	Hydrosulfuric acid (or hydrogen sulfide),	H_2S.
Hydrobromic acid,	HBr		
Hydriodic acid,	HI		

If the hydrogen in one or more molecules of these acids is replaced by a metal, we obtain a salt, named from the acid **by *dropping the prefix* and changing the termination into *-ide*:**

Thus HCl gives $NaCl$, sodium chloride;
$2\ HCN$ gives $Ca(CN)_2$, calcium cyanide;
H_2S gives K_2S, potassium sulfide.

26. What is the valence of the element or group combined with hydrogen in each of the five acids listed above?

27. Magnesium is *divalent*, and aluminum *trivalent* (§ 122). Give the names and formulas of the sodium, magnesium, and aluminum salts of each of the above five acids, indicating the valence of each metal and radical. *Follow the rule of valence.*

II. Chloric Group.

These acids have the **termination *-ic*,** without any prefix. They all contain oxygen.

Chloric acid,	$HClO_3$	Carbonic acid,	H_2CO_3
Cyanic acid,	$HCNO$	Oxalic acid,	$H_2C_2O_4$
Boric acid,	H_3BO_3	Sulfuric acid,	H_2SO_4
Nitric acid,	HNO_3	Chromic acid,	H_2CrO_4
Iodic acid,	HIO_3	Phosphoric acid,	H_3PO_4
Acetic acid,	$HC_2H_3O_2$	Arsenic acid,	H_3AsO_4

The names evidently tell us nothing about the number of atoms of oxygen in a molecule. *That has to be remembered separately for each acid.*

When the hydrogen of one or more molecules of one of these acids is replaced by a metal we obtain a salt; its name ends in ***-ate.***

$NaNO_3$, sodium nitrate; Na_2CO_3, sodium carbonate; Na_3PO_4, sodium phosphate.

28. What is the valence of the radical that combines with hydrogen to form each of the above acids? Write the names and formulas of the sodium, magnesium, and aluminum salts of the above acids, indicating the valence of each metal and radical.

III. Chlorous Group.

If an acid exists with *one less* **atom of oxygen** than the corresponding " -ic " acid, it is usually given a name ending in ***-ous.***

Chlorous acid,	$HClO_2$	Nitrous acid,	HNO_2
Sulfurous acid,	H_2SO_3	Phosphorous acid,	H_3PO_3*

---

* This acid is really $H_2(HPO_3)$ and its radical $(HPO_3)^{--}$, since but two of the three hydrogen atoms are replaceable by metals.

If the hydrogen of one or more molecules of one of these acids is replaced by a metal, we obtain a salt; its name ends in ***-ite.*** Example, $Ca(NO_2)_2$, calcium nitrite.

29. Write the names and formulas of the sodium, magnesium, and aluminum salts of nitrous and sulfurous acids, indicating the valence of each metal and radical.

IV. Hypochloric Group.

Occasionally we find an acid with *two less* **atoms of oxygen** than the corresponding "-ic" acid. This will have a name with the prefix ***hypo-***, in addition to the ending ***-ous.***

Hypochlorous acid,	$HClO$	Hypophosphorous acid,	H_3PO_2*
Hypoiodous acid,	HIO	Hyponitrous acid,	HNO

Their salts have the same prefix, ***hypo-***, with the termination ***-ite.*** Example, $KClO$, potassium hypochlorite.

30. What will be the names and formulas of the sodium, magnesium and aluminum salts of hypochlorous acid?

V. Perchloric Group.

We know a few acids that contain ***one more*** **atom of oxygen** than the corresponding "-ic" acid. These are given the prefix ***per-***, and the ending ***-ic.***

Perchloric acid,	$HClO_4$	Periodic acid,	HIO_4
		Permanganic acid,	$HMnO_4$†

Their salts have the prefix ***per-***, with the termination ***-ate.*** Example, $KMnO_4$, potassium permanganate.

31. Write the names and formulas of the sodium, magnesium, and aluminum salts of the acids of this group.

32. Write the names and formulas of five different acids containing chlorine, in the order of increasing content of oxygen. Write names and formulas of their ferrous and ferric salts.

The ending -Ous indicates lower		**amount of oxygen for an acid,**	**valence for a metal.**
The ending -Ic indicates higher			

---

* Only one of the three hydrogen atoms in this acid is replaceable by metals.

† In this and in a few other acids, the prefix does not have just the meaning that has been indicated.

Summary:

Acid	hydro-ic	hypo-ous	-ous	-ic	per-ic
Salt	-ide	hypo-ite	-ite	-ate	per-ate
Atoms of oxygen	0	$n-2$	$n-1$	n	$n+1$
Example	HCl	$HClO$	$HClO_2$	$HClO_3$	$HClO_4$

Get this summary well in mind. Then go back and review the entire section. Most of these formulas have been met before; hence it will not be difficult to commit all of them to memory. However, do not attempt to memorize them as *lists* of acids. That was worth while only when we were classifying acids according to activity (§ 103).

127. How to Develop Skill in Writing Formulas.—It must be remembered that valence is not the means by which formulas were first derived. The formula H_2O, for example, was not assigned to water because hydrogen has a valence of +1 and oxygen a valence of −2. On the contrary (1) the percentage composition of water was determined by experimental methods. (2) Its molecular weight was determined by weighing its vapor (§ 156). (3) The relative atomic weights of hydrogen and oxygen were then found by comparing the percentage compositions of a large number of the gaseous compounds of these elements (§ 159). Only then was it possible to work out the formula of water; and, as a matter of history, chemists came to agree upon this only after half a century of experiment and controversy.

By comparing the formulas of substances worked out *individually*, the idea of valence was developed. In its origin it was merely *a means for remembering formulas*, determined separately for the individual substances by laborious experiments—just as certain rules of spelling enable us to remember the forms which the individual words of our language have assumed, after centuries of use.

A little practice at this time will make the student so expert in writing formulas that he will have no more difficulty with that phase of the present course. As suggestions:

1. Learn the formulas of the common acids (§ 126). These will give you at once the valences of all the common non-metals and non-metallic radicals.

2. Learn the valences of the common metals, paying special attention to those that have more than one valence (§ 122).

3. Practice writing both names and formulas of salts, formed by combining metals with radicals, (§ 120).

4. If the reagent bottles on the laboratory side-shelf are marked with both names and formulas, check them over to determine whether these correspond to what would be predicted from the known valences of the elements and radicals concerned. Any substances of irregular formula should be separately noted.

128. Balancing Equations.—Equations that do not involve oxidation and reduction as well as many that do are very easy to balance.

1. Make sure that all formulas are correctly given, and that no substance has been omitted from either side of the equation.

2. Begin with some atom or group of atoms that occurs *in only one place*, in each side of the equation; then pass back and forth, from one side of the equation to the other, adjusting one element or group at a time.

Let us first balance an equation for the action of metallic aluminum on copper sulfate, forming aluminum sulfate and copper:

$$Al + CuSO_4 \rightarrow Al_2(SO_4)_3 + Cu$$

Having checked this over to make sure that all formulas are correct, we begin with the SO_4 groups. Three of these occur on the right-hand side of the equation; hence we adjust by writing.... .... $3CuSO_4$ on the left.

This gives us three copper atoms on the left, which we adjust by writing............ $3Cu$ on the right.

The aluminum still needs to be adjusted. Two aluminum atoms on the right require $2Al$, on the left. The balanced equation then stands:

$$2Al \quad + \quad 3CuSO_4 \quad = \quad Al_2(SO_4)_3 \quad + \quad 3Cu$$

Let us next balance the equation:

$$HI \quad + \quad HIO_3 \quad \rightarrow \quad H_2O \quad + \quad I_2.$$

The only element that occurs in only one place on each side of the equation is oxygen. On the left we have three oxygen atoms, which we adjust by writing..........$3H_2O$ on the right.

We then have six hydrogen atoms on the right, and on the left; only two. We therefore write............ $5HI$ on the left.

This, with the additional hydrogen atom in HIO_3, will make a total of six hydrogen atoms. We now have a total of six iodine atoms on the left, which is adjusted by writing ... .$3I_2$ on the right. The balanced equation then stands:

$$5HI \quad + \quad HIO_3 \quad = \quad 3H_2O \quad + \quad 3I_2$$

EXERCISES

1–32. Review the problems and exercises of this chapter.

33. Draw up a table with 100 squares in ten rows and ten columns, with space for headings at the top and in the left-hand margin. Head the top margin with the ten electro-positive ions, NH_4^+, Mn^{++}, Mg^{++}, Hg^+, Hg^{++}, Fe^{++}, Fe^{+++}, Sn^{++}, Sn^{++++}, H^+. In the left-hand margin list ten common electro-negative ions (including OH^-). Then fill in the 100 squares with the *names* and *formulas* of the 100 compounds that might be formed by combining the given ions.

34. Write and balance the following equations:

Ferric chloride + hydrogen sulfide = ferrous chloride + hydrogen chloride + S.
Potassium chlorate (gently heated) = potassium perchlorate + oxygen.
Ferric sulfate + zinc = ferrous sulfate + zinc sulfate.
Zinc + silver sulfate = zinc sulfate + silver
Ammonium sulfate + magnesium hydroxide = magnesium sulfate + water + ammonia.
Calcium phosphate + sulfuric acid = calcium sulfate + phosphoric acid

35. Draw up formal definitions of the following, based on this text; then compare with definitions given by the dictionary: Hydroxyl, valence, chemical formula, electron.

36. Explain and illustrate the difference between polar and non-polar valence.

CHAPTER X

CHEMICAL REACTIONS

If you interview a professional chemist on any subject in which chemistry plays a part, you will soon discover that he has developed a sort of "chemical instinct," which enables him to tell just about what will happen when stated substances are brought together in new ways, or under new conditions. To a very marked degree, he has acquired the ability to reason chemically.

Now, it is precisely this sort of ability that the student must acquire, in some limited degree, if the present course is to yield him anything of permanent value. Long after the details of formulas and equations have faded from memory, he should be putting chemistry to some use, in his business, home, or avocation. For if the chemical mode of thought has once been mastered, any library will supply the necessary chemical facts.

Concerning the manner in which practical ability of this sort may best be cultivated, note, first of all, that all chemical reasoning is based upon **general principles.** These include certain laws, and the explanations of these laws afforded by theories. (We now understand that theories are but the expression of our views of the mechanical make-up of the universe; and that they are the most practically useful things in science, because they penetrate the most deeply beneath the surface of phenomena, to get at the inner reasons why things happen as they do.) This course, then, is chiefly concerned with presenting a few fundamental laws and theories, and in showing how they may be applied.

Nevertheless, when we come to use these principles, we find that we must be guided by the properties of particular substances. Thus, the second part of our task is to become familiar with the most outstanding physical and chemical properties of a few important substances. We must learn to know these intimately, not merely by studying the text, but by actually working with them in the laboratory. In the present chapter (and in the laboratory work which will accompany it), we shall make a study of these common substances, *classified by properties.* Then, in later chapters, we shall meet them again, *classified by elements.*

It is very important that the student work all the exercises of the present chapter, one by one, as he comes to them.

129. Complementary Properties.—Review § 50. It used to be the fashion to speak of chemical substances as reacting when they possessed an "affinity" for each other; and as failing to react, in the contrary case. To-day, however, "affinity" has come to acquire a highly technical meaning, which would lead us too far afield if we should attempt to explain it. For our present purposes, it is sufficient to think of chemical reactions as occurring **when conditions are favorable,** provided the substances brought together have what we might call **complementary properties.** One must be an acid, the other a base; or one a metal, the other a non-metal; or one an oxidizing agent, the other a reducing agent; or one the salt of a volatile acid, the other a non-volatile acid; or one must contain the metallic part, the other the non-metallic part of a desired precipitate.

1. Write an equation to illustrate a reaction that may be expected to occur in each of these cases.

Thus, when one is asked what will happen when specified substances are brought together, the first step is to recall their properties, and try to recognize among these a pair of complementary properties. (A chemical property may or may not have a definite *name*.) If the given substances are somewhat uncommon, they may still be known to resemble other substances, whose properties are already familiar. Thus, from the reaction of chlorine with sodium hydroxide (§ 184), anyone with a little chemical experience may draw conclusions concerning the reaction of bromine with potassium hydroxide. This is **chemical reasoning by analogy.** It becomes reliable only when one has studied chemistry for a considerable length of time. One never attempts to reason from mere formulas, except in so far as *structural formulas* may recall and suggest reactions.

2. Name or describe the complementary properties possessed by the members of the following pairs of substances:

PbO	SO_3
H_2S, § 231	O_3
Cl_2, § 183	Hg
$KMnO_4$, § 517	SO_2, § 236
$NaCl$	$AgNO_3$

130. Oxidation and Reduction.—Oxidation and reduction have much broader meanings than those indicated by the preliminary definitions of § 55. From the most general point of view, **oxidation** is any process that results in an algebraic increase in valence (namely, in valence becoming more positive or less negative). **Reduction** is any process that results in an algebraic decrease in valence (namely, in valence becoming less positive, or more negative). In applying these definitions, we look upon an uncombined element (Hg, Zn), or one combined only with itself (Cl_2, N_2) as having a valence of zero.

Thus, when zinc burns in an atmosphere of chlorine, zinc chloride is produced:

$$Zn + Cl_2 = Zn^{+2}Cl_2{}^{-1}.$$

Here zinc is considered to be oxidized, since it increases in valence from 0 to +2. Chlorine, on the other hand, is reduced, since it decreases in valence from 0 to −1.

3. Which element (§ 121) is oxidized and which reduced in each of the following reactions?

$$S + Fe = FeS$$

$$Zn + 2HCl = ZnCl_2 + H_2$$

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

131. Oxidation and Reduction in Terms of Electrons.—In sodium-ion, as a constituent of NaCl or NaOH, the valence of sodium is +1, as compared with a valence of 0 in uncombined, metallic sodium. But sodium-ion, Na^+, had been explained (§ 125) as a sodium atom which has parted with one electron. Accordingly, each increase of valence, on the part of an atom or radical, is caused by the loss of a corresponding number of electrons; and each decrease of valence by the gain of a corresponding number of electrons.

Oxidation:	Valence increased	Electrons lost
Reduction:	Valence decreased	Electrons gained

4. Explain (§ 125) in terms of electrons, how chloride-ion, Cl^-, differs from an atom of uncombined chlorine.

5. Compare the valence of chlorine in chloride-ion with its valence in uncombined chlorine.

6. Is a process that results in the conversion of elementary chlorine into chloride-ion to be considered as oxidation or reduction? What would the reverse process be?

7. State what transfers of electrons take place in the reactions of question 3.

8. Which element is oxidized and which reduced in the electrolysis of water?

It is worth noticing that **oxidation and reduction always go on together.** One atom or group of atoms loses electrons (is oxidized), while another atom or group of atoms gains electrons (is reduced). An **oxidizing agent** is something that can oxidize something else (namely, deprive something else of electrons). In the process, the oxidizing agent is itself *reduced.* A **reducing agent** is something that can reduce something else (namely, cause something else to accept electrons). In the process, the reducing agent is itself *oxidized.*

The terms " oxidizing agent " and reducing agent are purely relative ones. In the presence of sufficiently powerful oxidizing agents, most substances can be oxidized, and are thus made to serve as reducing agents; and in the presence of sufficiently active reducing agents, most substances can be reduced, and are thus made to serve as oxidizing agents. Ordinarily, a substance is not classified as an oxidizing or reducing agent if it manifests its oxidizing or reducing properties only in the presence of extremely active substances of the opposite kind.

132. Oxidizing Agents.—The following are important oxidizing agents:

I. Elementary Oxygen and Ozone.—Elementary oxygen reacts with many substances even at room temperature. Thus, yellow phosphorus, in finely divided condition, catches fire when exposed to the air; and solutions of ferrous salts are oxidized by the air to ferric salts. Ozone oxidizes many substances under conditions such that ordinary oxygen would have no effect.

II. Hydrogen peroxide (H_2O_2). Review § 90.

III. The halogens. This is a general name given to the elements fluorine, chlorine, bromine, and iodine. These are among the most effective oxidizing agents. They decrease in activity in the order given. Read § 199.

9. Give an equation to illustrate the action of chlorine as an oxidizing agent, and show that the chlorine is itself reduced.

10. Tell what transfer of electrons takes place in the equation just cited.

IV. Nitric acid and concentrated sulfuric acid. These are the so-called *oxidizing acids*; but, from the most general point of view, any acid is an oxidizing acid, since any metal that reacts with an acid thereby has its valence increased.

11. Show that this is true for zinc, reacting with hydrochloric acid.

V. Chromates, dichromates, and permanganates. When these salts serve as oxidizing agents, they are themselves reduced, commonly to chromium salts (valence of Cr, +3) and manganese salts (valence of Mn, +2).

12. Write the formulas of ammonium chromate, dichromate, and permanganate.
13. What is the valence (§ 121) of the chromium or manganese, in each case?

VI. Hypochlorites and hypobromites. Solutions of these salts are commonly used as bleaching agents.

14. Write the formulas of the magnesium salts.

VII. Ferric and mercuric salts. These are quite readily reduced to ferrous and mercurous salts, and accordingly serve as oxidizing agents.

15. Give the valence (§ 122) of the metal, in each case, in the original (oxidized) condition, and in the final (reduced) condition.

VIII. Nitrates, chlorates, perchlorates, and peroxides. These are commonly used as oxidizing agents in the dry condition, mixed with oxidizable material. (Such mixtures are often dangerously explosive, (§ 206).

16. Write the formulas of the sodium compounds.

IX. Oxides of the heavy metals. A few metals form more than one stable oxide. In such cases, the oxide in which the metal shows a high valence is commonly a very pronounced oxidizing agent. Examples: Manganese dioxide, MnO_2; lead dioxide, PbO_2; red lead oxide, Pb_3O_4. Oxides of heavy metals near the bottom of the electrochemical series are oxidizing agents, since they are readily reduced to metal by many reducing agents.

17. Give the formulas of three such oxides.

133. Reducing Agents.—The following are important reducing agents:

I. Hydrochloric acid, hydrobromic acid, and hydriodic acid. Hydrochloric acid acts as a reducing agent only in the presence of very pronounced oxidizing agents, such as manganese dioxide.

(§ 180). Hydrobromic acid is a more active reducing agent. Hydriodic acid is more active still. Whenever these substances serve as reducing agents, they are themselves oxidized to the corresponding free halogen (Cl_2, Br_2, I_2).

18. What change of valence takes place, in each case?

II. Hydrogen sulfide. When hydrogen sulfide serves as a reducing agent, it is itself oxidized to sulfur (by mild oxidizing agents) or sulfuric acid (by active oxidizing agents).

19. What change of valence takes place, in each case?

III. Sulfurous acid and its salts (sulfites). When these serve as reducing agents, they are themselves oxidized to sulfuric acid and its salts (sulfates).

20. What is the change of valence?

IV. Ferrous salts, mercurous salts, and stannous salts. These are readily oxidized to the corresponding ferric, mercuric, and stannic salts.

21. What change of valence (§ 122) takes place in each case?

V. Arsenious acid and its salts (arsenites). When these serve as reducing agents they are themselves oxidized to arsenic acid and its salts (arsenates).

22. What change takes place in the valence of arsenic?

VI. Many metals (especially those toward the top of the electrochemical series). Thus, sodium (or sodium amalgam, which is an alloy of sodium with mercury, § 561) is an important reducing agent in many laboratory operations in organic chemistry.

At higher temperatures, metallic magnesium or aluminum are vigorous reducing agents. Read § 178.

23. What weight of metallic aluminum is needed to reduce one mole of ferric oxide? What weight of metallic iron will be formed?

VII. Carbon, and other readily oxidizable non-metals. When an excess of carbon is thus employed as a reducing agent, it is oxidized to carbon monoxide. Sulfur is oxidized to sulfur dioxide (or sulfurous acid) by mild oxidizing agents, and to sulfur trioxide (or sulfuric acid) by vigorous oxidizing agents.

24. Write and balance an equation for the reduction of lead dioxide to metallic lead, by carbon.

25. What is the relationship (§ 104) of sulfur dioxide to sulfurous acid, and sulfur trioxide to sulfuric acid?

26. Indicate several oxidizing agents with which powdered sulfur may be mingled, to form an explosive mixture.

27 Recall a lecture experiment to illustrate the action of hydrogen as a reducing agent.

VIII. Carbon monoxide (at higher temperatures). This is the most important industrial reducing agent, since it is responsible for the production of iron from iron ore, in the blast furnace (§ 492).

28 To what product is carbon monoxide oxidized, when it serves as a reducing agent?

29. How many moles of carbon monoxide are needed to reduce one mole of ferric oxide to metallic iron?

30. Write and balance an equation for the reduction of magnetic iron oxide to iron, by means of carbon monoxide.

IX. Many compounds and materials rich in carbon and hydrogen. Formaldehyde and alcohol are excellent reducing agents, even in solution; and powdered starch, sugar, coal, or sawdust will reduce many of the oxides of the heavy metals to metal, when mixed with these oxides and heated.

31. If an excess of the oxidizing agent is employed, what products will be formed (§ 40)?

32. Write and balance an equation for the reaction between alcohol vapor, C_2H_5OH, and hot copper oxide

33. What products would one expect to obtain on heating calcium carbide (CaC_2) with an excess of copper oxide?

134. Types of Reactions. In seeking to determine what sort of reaction is likely to take place in any given instance, it is often helpful to recall the most common types of reactions:

I. Direct union.

34. Write equations to illustrate direct union of a metal with a non-metal, of a metallic oxide with a non-metallic oxide, and of a salt with water (§§79, 112).

II. Decomposition. This is the reverse of direct union.

35. Write equations for the decomposition of two substances that yield oxygen when heated.

III. Displacement.

36. Which metals displace hydrogen from dilute acids?

37. Write and balance an equation for the displacement of hydrogen from acetic acid, by zinc.

38. Under what conditions (§ 112) will one metal displace another from the salts of the latter?

IV. Other cases of oxidation and reduction. Examples are given in the next section (§ 135).

39. Show that the three preceding cases all involve oxidation and reduction.

V. Double decomposition.

40. Define double decomposition (§ 112).

41. Write an equation for the preparation of a volatile acid from one of its salts, by double decomposition

42. Write an equation for the preparation of an insoluble salt, by double decomposition.

VI. Ionization.

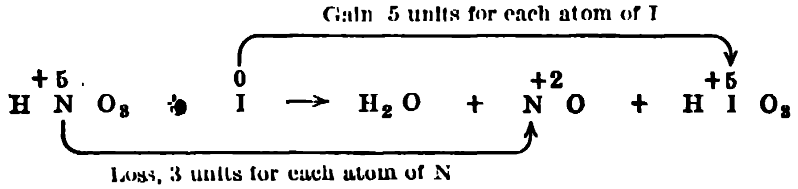
43. Write equations showing the ionization of an active and an inactive acid, respectively.

135. Balancing Equations Involving Oxidation and Reduction. Equations involving oxidation and reduction are best balanced by taking note of the changes in valence that are involved. A brief study of the method should be made at this time; though extended practice in its application may well be postponed until much later in the course.

(1) For example, consider the oxidation of iodine to iodic acid by means of nitric acid. The unbalanced formulation may be written:

$$HNO_3+I \rightarrow H_2O+NO+HIO_3.$$

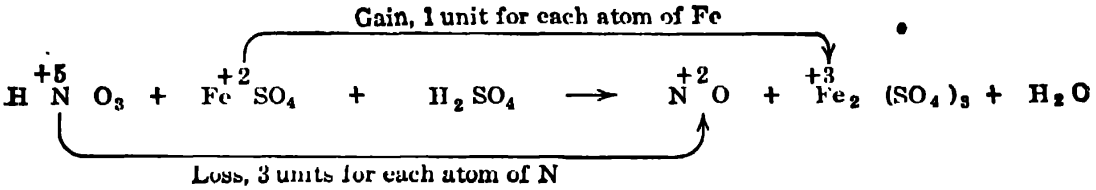
Next find two elements that change valence as a result of the reaction and note what change in valence takes place (§ 121).


Gain 5 units for each atom of I
+5
0
+2
+5
H N O₃ + I → H₂O + N O + H I O₃
Loss, 3 units for each atom of N

An uncombined element is assumed to have a valence of zero. In the reaction above, iodine has been oxidized, each atom *increasing* in valence by 5 units, from 0 to +5. The nitrogen has been reduced, each atom *decreasing* in valence by 3 units, from +5 to +2. But the units of valence *lost* by one kind of atom must thus be equal to the units *gained* by the other kind. Accordingly, we must take $5HNO_3$ (which is a loss of $5\times3=15$ units) and 3I (which is a gain of $3\times5=15$ units). This will then give us 5NO and $3HIO_3$ in the right-hand member of the equation. Everything is now balanced but water; and by counting atoms of H or O we see that there can be but one molecule of this. The balanced equation then stands:

$$5HNO_3+3I=H_2O+5NO+3HIO_3.$$

(2) Consider next the reduction of nitric acid to nitric oxide by ferrous sulfate in the presence of sulfuric acid (§ 303):


Gain, 1 unit for each atom of Fe
Loss, 3 units for each atom of N

$$H\overset{+5}{N}O_3 + \overset{+2}{Fe}SO_4 + H_2SO_4 \longrightarrow \overset{+2}{N}O + \overset{+3}{Fe_2}(SO_4)_3 + H_2O$$

To balance, we must make the gain equal to the loss; therefore $6FeSO_4$ and $2HNO_3$. This will produce 2NO and $3Fe_2(SO_4)_3$. We then have nine SO_4 groups, on the right. On the left, $6FeSO_4$ furnishes only six SO_4 groups. We therefore need $3H_2SO_4$; which, with the $2HNO_3$, will furnish enough hydrogen for $4H_2O$. Thus, the final result is

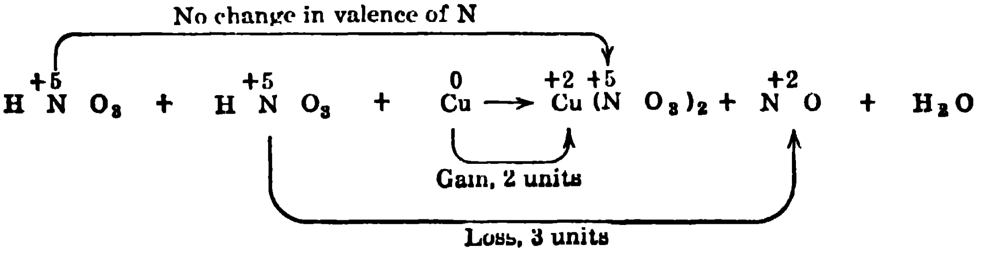
$$2HNO_3+6FeSO_4+3H_2SO_4=2NO+3Fe_2(SO_4)_3+4H_2O.$$

To verify the result we count atoms of O and find 42 in each member of the equation. **One should never fail to check the work in this way, with an element not previously used in arriving at a balance.**

(3) When copper dissolves in fairly dilute nitric acid (§ 294) we have:

$$HNO_3+Cu=Cu(NO_3)_2+NO+H_2O.$$

Here a complication is introduced by the fact that nitrogen, the element reduced, *appears in two different places in the right-hand member of the equation.* To meet this difficulty *we write* HNO_3 *twice in the left-hand member* and treat the two as two different substances, one producing $Cu(NO_3)_2$, the other NO:



$$H\overset{+5}{N}O_3 + H\overset{+5}{N}O_3 + \overset{0}{Cu} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}O_3)_2 + \overset{+2}{N}O + H_2O$$

Comparing the gain and loss we get $2HNO_3$ and 3Cu. This gives $3Cu(NO_3)_2$ and 2NO. But as soon as we have written $3Cu(NO_3)_2$ we see that we need an additional $6HNO_3$ to furnish the nitrate groups; and by counting H atoms we see that we need $4H_2O$. The balanced equation is therefore

$$8HNO_3+3Cu=3Cu(NO_3)_2+2NO+4H_2O.$$

A check is furnished by counting atoms of oxygen—24 on each side.

The method we have outlined will apply as well to equations involving oxidation and reduction of organic compounds; though the valences that will then need to be indicated for carbon are not the ones that an organic chemist would assign to that element.

44. Balance:

$$KMnO_4+H_2SO_4+H_2C_2O_4 \rightarrow K_2SO_4+MnSO_4+H_2O+CO_2.$$

136. Degree of Completeness of Chemical Reactions.—We have just been considering *what kind* of products will be obtained in a reaction between given chemical substances. Of equal importance is the question of *how complete* the reaction will be. Reactions become practically complete:

(*a*) When the reactants are extremely active. Thus, when a very active oxidizing agent, such as chlorine, is brought into contact with a very active reducing agent, such as hydrogen sulfide, we may know in advance that the reaction will be complete. Again, a very active acid, such as hydrochloric acid, reacts completely with a very active base, such as sodium hydroxide. (Otherwise expressed, the reverse reaction, hydrolysis of sodium chloride, fails to take place.)

(*b*) When one or more of the products of the reaction are but slightly active; for example, when a slightly active acid or base is formed from one of its salts.

45. Write equations to illustrate.

(*c*) When a substance is formed that is insoluble in the solvent used, and separates as a precipitate, thus preventing the reverse reaction from taking place.

46. Illustrate.

(*d*) When a gas is formed, which escapes from the solution.

47. Illustrate.

Whenever a reaction is incomplete, it may be made somewhat more nearly complete if a large excess of one of the reacting substances is used. Thus, hydrogen gas and iodine vapor combine to a slight extent when they are heated, forming hydrogen iodide:

$$H_2+I_2 \rightleftarrows 2HI.$$

The reaction becomes much more nearly complete; that is, a much larger proportion of the iodine is made to combine, *other things being equal*, if we use a large excess of hydrogen; and a much larger proportion of the hydrogen, other things being equal, if we use a large excess of iodine. We shall make repeated use of this principle (§§ 217, 266).

137. How to Translate Molecular Equations into the Ionic Form.—Ordinary equations, expressing chemical reactions in terms of reacting molecules, rather than in terms of ions, are often referred to as **molecular equations.**

$$AgNO_3+NaCl=AgCl\downarrow+NaNO_3.$$

In this particular case, however, the two reactants were probably almost completely ionized, as they originally existed, in separate solutions; and the sodium nitrate that is formed remains in solution and is therefore ionized. If we replace each of the ionized substances by the formulas of its ions, the equation becomes:

$$Ag^++NO_3^-+Na^++Cl^-=AgCl\downarrow+Na^++NO_3^-.$$

Now, sodium-ion and nitrate-ion are common to both sides of the equation. We may accordingly cancel them out, and thus obtain a simplified **ionic equation**:

$$Ag^++Cl^-=AgCl\downarrow.$$

Thus we see that the essential reaction occurring here is the *direct union* of ions to form molecules of an insoluble salt. The reaction does not really produce sodium nitrate at all; for the separate ions, Na^+ and NO_3^-, were present as such in the two solutions before mixing, and, after mixing still remained almost entirely uncombined. Still, **we often speak of a reaction as forming a certain product, when we merely mean that a solution results which contains ions derived from that product.** Thus, when we say that an acid reacts with a base to form a *salt* and water, we merely mean that when the reaction has taken place the solution will be found to contain the ions of a particular salt. In reality, one of those was already present in the base, and other in the acid, *previous to mixing the acid with the base.* The only new product resulting from the reaction is accordingly water:

$$H^+ + OH^- = HOH.$$

48. Write an equation for the neutralization of hydrochloric acid by sodium hydroxide; then, assuming that water is not appreciably ionized, translate the equation into ionic form, and show that it reduces to the equation just given.

49. Write the equation for the reaction of zinc with sulfuric acid, and translate it into ionic form. Then state in what sense it is true that "zinc reacts with sulfuric acid to form zinc sulfate and hydrogen."

Summary: **To translate an ordinary (molecular) equation into ionic form, replace the formula of every largely ionized substance by the formulas of its ions** (remembering that only soluble salts, and soluble, *active* acids and bases are largely ionized). **Then cancel out all ions common to the two sides of the equation.**

50. Write an equation for the reaction of iron with hydrochloric acid, to form ferrous chloride. Translate this into ionic form. What transfer of electrons is indicated by this ionic equation?

51. Write ionic equation for the precipitation of metallic copper from a copper sulfate solution by the action of metallic iron, the other product being ferrous sulfate.

52 Write ionic equation for the action of chlorine on potassium bromide solution, the chlorine *displacing* the bromine.

53. Write ionic equation for the reduction of ferric chloride to ferrous chloride by means of metallic zinc, the other product being zinc chloride.

54. In what sense is the preceding reaction one of oxidation and reduction? Tell what transfers of electrons take place.

Whenever we have to deal with a substance that is only slightly ionized, the **general result of the reaction** may be obtained by treating the substance as if it were not ionized at all. Thus, when sodium hydroxide solution is poured into acetic acid, the reaction is:

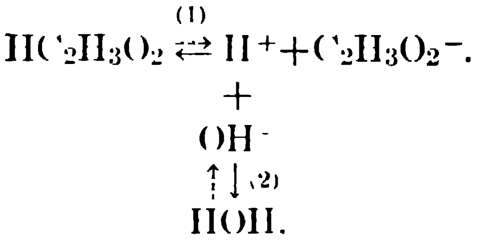
$$HC_2H_3O_2 + NaOH = NaC_2H_3O_2 + H_2O.$$

The formulas of the base and salt may here be replaced by their respective ions; but water and acetic acid (a slightly active acid) should be treated as if they were not ionized. Then, on canceling out Na^+ (which is common to both sides of the equation) we obtain:

$$HC_2H_3O_2 + OH^- = C_2H_3O_2^- + H_2O.$$

The *general result* of the reaction is thus the same as if hydroxyl ions had reacted with acetic acid molecules, to form acetate ions, and water.

We should remember, however, that this general result is really accomplished in two steps: (1) Dissociation of acetic acid molecules, a few at a time (depending on the rate at which the base is being added), thus maintaining a very slight concentration of hydrogen-ion, until the very last. (2) Direct union of hydrogen-ion, practically as fast as formed, with the hydroxyl-ion that is being added:



$$\begin{array}{ccc} HC_2H_3O_2 \overset{(1)}{\rightleftarrows} & H^+ & +C_2H_3O_2^-. \\ & + & \\ & OH^- & \\ & \uparrow\downarrow{\scriptstyle (2)} & \\ & HOH. & \end{array}$$

In what follows, we shall sometimes be chiefly interested in the general result of a reaction, and sometimes in the separate steps by which such a general result is accomplished.

55. Put the general result of the following reaction into ionic form, distinguishing carefully between ferrous- and ferric-ion, and remembering that hydrogen sulfide is only very slightly active:

$$2FeCl_3+H_2S=2FeCl_2+2HCl+S.$$

56. Indicate the two steps in which the general result just obtained is accomplished.

138. Ionic Representation of Certain Types of Reactions.—It is now possible for us to review some reactions which have previously been put in molecular form, to see how they would be represented if considered from the ionic point of view:

(*a*) **Action of a metal on an acid.**—The metal reacts with hydrogen-ion, to produce metallic-ion and hydrogen gas:

$$Zn+2H^+=Zn^{++}+H_2.$$

57. Show that this is the general result of the reaction of metallic zinc with any active, non-oxidizing acid.

58. Explain the preceding reaction as a transfer of electrons.

(*b*) **Neutralization of an acid by a base.**—If the acid and base are both active, the general result of the reaction is the *direct* *union* of hydrogen-ion with hydroxyl-ion, to form water. (See § 137.)

59. Show that this is true for the neutralization of calcium nydroxide by nitric acid.

(*c*) **Hydrolysis of a salt.**—The general result of hydrolysis is as if water reacted with one of the ions of the salt, to form a slightly ionized acid or base.

60. Show that this is true for the hydrolysis of sodium fluoride. (Remember that hydrofluoric acid is but slightly ionized.)

(*d*) **Double decomposition.** From the point of view of the ionic theory, double decomposition is not double replacement (§ 112) at all. The general result of such a reaction, between active substances at least, is always *direct union of ions*, to form molecules of an insoluble or slightly active substance.

61. Show that this is true for the double decomposition resulting in the formation of a precipitate of barium sulfate.

62. Show that it is true for the action of dilute hydrochloric acid on a solution of sodium acetate. (Remember that acetic acid is but slightly active.)

63. Explain why the preceding reaction is reasonably complete, even at room temperatures, in dilute solutions.

EXERCISES

Balance the following:

64. $KMnO_4+HCl \rightarrow KCl+MnCl_2+H_2O$.

65. $HNO_3+H_2S \rightarrow H_2SO_4+NO_2+H_2O$.

66. $HNO_3+P \rightarrow H_3PO_4+NO_2+H_2O$.

67. $H_2S+KMnO_4+HCl \rightarrow KCl+MnCl_2+H_2O+S$.

68. $H_2S+K_2Cr_2O_7+HCl \rightarrow KCl+CrCl_3+H_2O+S$.

69. $SnCl_2+HgCl_2 \rightarrow SnCl_4+HgCl$.

70. $FeCl_2+K_2Cr_2O_7+HCl \rightarrow KCl+CrCl_3+FeCl_3+H_2O$.

1. $KIO_3+KI+HC_2H_3O_2 \rightarrow KC_2H_3O_2+H_2O+I_2$.

CHAPTER XI

CHEMICAL ARITHMETIC

Whenever one attempts to apply chemistry in a useful way, one is confronted with the question of what sort of substances or materials to bring together, in order to obtain a desired result. The first part of the preceding chapter is an attempt to show how a trained chemist approaches a question of this kind. Then, after one has decided *what sort* of reactants to employ, there is the further question of *how much* of each. No one can hope to put his chemistry to any practical use until he can solve this question, too Almost every laboratory operation needs to be preceded by a simple calculation, to determine what relative weights or volumes should be taken. Actually, the arithmetic called for is of a very easy kind. We have already met a number of problems of this sort, and now need only pause to become conscious of the method by which we solved them.

139. Standard Conditions. Molar Volumes.- The volume of any given mass of gas depends on the conditions of temperature and pressure under which it is measured (§ 20). It is, therefore, customary to state the volume which the gas would have at **standard conditions,** namely at a temperature of 0° C., under a pressure of 760 mm. of mercury.*

A liter of oxygen gas, under standard conditions, weighs 1.429 g. Therefore, one mole of oxygen (32 g.), under standard conditions, occupies $32 \div 1.429 = 22.4$ liters. Now, under like conditions, equal numbers of molecules - and therefore equal numbers of moles—of all gases occupy equal volumes. Accordingly, **one mole of any gas or vapor, recalculated to standard conditions,† occupies very nearly 22.4 liters.** This is called the **standard molar volume,** or sometimes the **gram-molecular volume.** We shall make constant use of it in what follows.

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* By this we mean that the pressure under which the gas is confined must be equal to the pressure that the atmosphere exerts, when supporting a column of mercury 760 mm. high, in a barometer.

† We say "recalculated to standard conditions," rather than "at standard conditions," because the gas might condense to a liquid or solid if an attempt were made actually to observe it at standard conditions. Still, we can calculate what the volume *would have been* if the gas had remained a gas, and obeyed the Laws of Charles and Boyle, throughout the whole range of temperature and pressure necessary to bring it to standard conditions (§ 158).

1. What is meant by a mole? Explain why a mole of oxygen is 32 g., rather than 16 g.

2. What is the weight of one mole of ammonia, NH_3? What volume does this occupy at standard conditions? Then what is the weight of one liter of ammonia, at standard conditions?

3. State how one may determine the weight, under standard conditions, of a liter of any gas whose formula is known. (See preceding question.)

4. Calculate the weight of a liter of chlorine, Cl_2, under standard conditions.

140. Converting Weights and Volumes into Moles.—Review §§ 38, 42. Though the weights and volumes of reacting substances are commonly given in units of the metric system, the chemist nearly always reasons in terms of moles. To convert any given **weight,** expressed in grams, into moles, divide by the molecular weight.

$$\frac{\text{Weight (g.)}}{\text{Mol. wt.}} = \text{moles.}$$

5. How many moles in 0.1901 g. of sulfuric acid?

6. How many moles in 36.468 mg. of hydrogen chloride?

If we wish to know how many moles correspond to a given **volume** of a substance, we may use either of two methods:

(1) If we know the **density** * of the substance, we may multiply the volume by the density to obtain the total weight, and then divide this by the molecular weight, to obtain the number of moles.

$$\frac{\text{Volume (cc.)} \times \text{density (g. per cc.)}}{\text{Mol. wt.}} = \text{moles.}$$

7. How many moles in one liter of water?

8. If the density of pure alcohol, C_2H_5OH, is 0.9, how many moles in 100 cc.?

9. How many cubic centimeters of solid calcium carbonate, density 2.8 g. per cc. are necessary for one mole?

10. Carbon dioxide, under unspecified conditions, has a density of 2 g. per liter. How many cubic centimeters of the gas, under these conditions, are needed to make 0.1 mole?

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* **Density** is the weight of unit volume. **Specific gravity** is relative weight, in comparison with some reference substance. If the reference substance is water, at 4° C., then specific gravity is numerically the same as density, and the two words may be used interchangeably.

(2) If the substance is a **gas or vapor** (not otherwise), each mole will occupy 22.4 liters, recalculated to standard conditions. Accordingly,

$$\frac{\text{Vol. of a gas or vapor (liters, stand. conds.)}}{22.4} = \text{moles}.$$

11. How many moles of ethylene are contained in 1000 liters of that gas, under standard conditions?

12. Express 112 cc. of hydrogen gas, under standard conditions, as a decimal part of a mole.

13. How many liters in a cubic meter (§ 33)? What total number of moles of all the constituents of coal gas (§ 347) is contained in one cubic meter of coal gas, under standard conditions?

141. Problems Based on Equations.—Problems based on chemical equations are solved in four steps, best explained by an example:

What volume of carbon dioxide gas may be obtained by the reaction between 5 g. of calcium carbonate and an excess of hydrochloric acid?

(1) **Write the equation, and make sure that it is correctly balanced:**

$$CaCO_3+2HCl=CaCl_2+H_2O+CO_2.$$

(2) **Pick out the weights or volumes mentioned in the statement of the problem.** Make note of these just *above* the formulas of the corresponding substances; and convert the one that is known into moles:

$$\underset{\substack{5\div 100=\\ 0.05\text{ mole.}}}{\overset{5\text{ g.}}{CaCO_3}}+2HCl=CaCl_2+H_2O+\overset{?\text{ l.}}{CO_2}.$$

(The molecular weight of calcium carbonate is 100.)

(3) **Reason from the equation.** It shows that one mole of calcium carbonate produces one mole of carbon dioxide. Therefore, 0.05 mole of calcium carbonate will produce 0.05 mole of carbon dioxide.

(4) **Convert the number of moles just obtained into a weight or a volume, as the problem may demand.** The problem calls for liters of gas (a volume). Accordingly, each mole of carbon dioxide, under standard conditions, will be 22.4 liters; and 0.05 mole will be 0.05×22.4 = 1.12 liters, *Ans.*

Another example:

What weight of hydrogen chloride is needed to react with calcium carbonate, to produce 10 *liters of carbon dioxide gas, under standard conditions?*

(1) Write and balance the equation. It is the same as in the preceding problem.

(2) Above the proper formulas, set down the indicated quantities, and convert the one that is known (10 liters of gas) into moles, by dividing by 22.4. The work then stands:

$$\begin{array}{l} \qquad\quad ?\ \text{g.} \qquad\qquad\qquad\qquad\qquad\qquad 10\ \text{l.} \\ CaCO_3+2HCl=CaCl_2+H_2O+CO_2. \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 10\ \ 22.4= \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad 0.4464\ \text{mole.} \end{array}$$

(3) Reason from the equation. It shows that each mole of carbon dioxide requires 2 moles of hydrogen chloride. Then 0.4464 mole of carbon dioxide will require 2×0.4464 = 0.8928 mole of hydrogen chloride.

(4) The problem demands that the number of moles just obtained shall be converted into a weight. Each mole of hydrogen chloride is 36.468 g. (Check this.) Accordingly, 0.8928 mole will be 0.8928×36.458 g. = 32.56 g., *Ans.*

14. Show what difference would have been made, in working the preceding problem, if 10 g. of carbon dioxide had been required, rather than 10 l.

142. Problems Involving Only the Volumes of Gases.—If a problem involves only the **relative volumes of gases,** the work is very much simplified, in that it is not necessary to convert these volumes into moles. Thus, in the equation,

$$2NH_3+3Cl_2=6HCl+N_2,$$

2 moles of ammonia require 3 moles of chlorine, to give 6 moles of hydrogen chloride and 1 mole of nitrogen. Now, equal numbers of moles occupy equal volumes; hence, the actual *volumes* of these gases will be in the same ratio of as the *numbers of moles.* Two liters of ammonia will react with 3 liters of chlorine, to give 6 liters of hydrogen chloride and 1 liter of nitrogen, under any given constant conditions.

15. What volume of ammonia will be needed to react with 15 cu. ft. of chlorine, and what volume of each of the two reaction products will be obtained?

16. If 15 cc. of ammonia are mixed with 15 cc. of chlorine, which gas is present in excess? How many cubic centimeters of that gas will be left unchanged at the end of the reaction?

17. What increase or decrease in volume will take place when 20 cc. of ammonia react with the relative amount of chlorine expressed by the equation?

143. How to Check Results.—As an illustration of a method that may be used to check results, refer to the problem at the close of § 141. The steps are:

1. Above the corresponding formulas, write the given weight or volume, and the final answer: 10 l. and 32.56 g. Be sure to designate the units used.

2. Below these formulas translate the number of moles indicated by the equation into **the same units.** One mole of CO_2 is 22.4 l. Two moles of HCl are 2×36.468 = 72.936 g. The work then stands:

$$\begin{array}{ccccc} & 32.56\text{ g.} & & & 10\text{ l.} \\ CaCO_3 + & 2HCl & = CaCl_2 + H_2O + & & CO_2 \\ & 72.936\text{ g.} & & & 22.4\text{ l.} \end{array}$$

3. Now multiply, criss-cross: 32.56×22.4 = 729.34; and 72.936 ×10 = 729.36. The practical identity of these two products indicates that the numerical work employed in solving the problem is very probably correct, though the same mistake in reasoning may have occurred both in the solution and in the proof. **Make sure that the two products agree as to decimal point.** This check is based on the rule of proportion that "the product of the means equals the product of the extremes."

18. Check the answer that was obtained for the first problem in § 141.

144. Some Common Causes of Trouble.—Trouble in solving problems is usually due to one of four things:

1. **Failure to balance the equation correctly,** or failure to interpret it correctly, when balanced. Note that 2HCl means two moles of hydrogen chloride; but H_2 is *one* mole of hydrogen, and occupies 22.4 liters, not twice that volume.

2. **Failure to use the proper units.** Remember that a *weight*, in the metric system, is commonly expressed in grams— never in cubic centimeters or liters.

3. **Failure to distinguish between the volume of a gas and the volume of a solution.** Remember that H_2S stands for 22.4 liters of hydrogen sulfide gas, under standard conditions. Dissolved in water, it may make an entirely different volume of solution.

4. **Failure to check the answer,** to see if it looks reasonable.

The remaining topics of this chapter may be postponed, to be presented later in the course, as called for by current laboratory work.

145. Problems Involving Only Relative Weights.—If a problem involves only **relative weights,** the unit of weight may be anything we please. Thus, the equation,

$$\begin{array}{ccccc} CaCO_3 & + & 2HCl & = & CaCl_2+H_2O+CO_2, \\ 40+12+48 & & 2\times 36.468 & & \\ =100 & & =72.936 & & \end{array}$$

indicates that the weight of hydrogen chloride required to react with the calcium carbonate is smaller than the weight of the calcium carbonate itself, in the ratio $\frac{2HCl}{CaCO_3}=\frac{72.936}{100}$; no matter whether the unit of weight concerned is the gram, pound, or ton. To get the weight of hydrogen chloride required to react with a certain weight of calcium carbonate, we therefore need only multiply the latter by the numerical value of the ratio 2HCl $CaCO_3$. Thus 5 lbs. of calcium carbonate will react with $5\times\frac{72.936}{100}=3.647$ lbs. of hydrogen chloride.

Tables of such **ratios of reacting weights,** often called **chemical factors,** are found in many chemical handbooks, and save one the trouble of calculating the molecular weights of the individual substances concerned, for only ratios of weights are needed.

19. What weight of hydrogen chloride will be needed to react with 40 mg. of calcium carbonate?

20. How many grams of hydrogen chloride will one kilogram of calcium carbonate require?

21. The chemical factor $SO_3/BaSO_4$ has what numerical value? Show how it may be used to find the percentage of sulfur trioxide in a compound, one gram of which will produce 0.2400 g. of barium sulfate.

145.—Problems Involving the Percentage Strengths and Densities of Reagents.—By the **percentage strength** of a solution we mean the number of grams of a specified dissolved substance in 100 g. of *solution*. Thus, a 40 per cent solution of hydrochloric acid contains 40 g. of hydrogen chloride for every 60 g. of water, to make 100 g. of solution. Very often the percentage strength of a solution is known from the way in which it was prepared. At other times, we may deduce the percentage strength from an observation of the boiling point, freezing point index of refraction, density, or some other property, whose variation with varying percentage strength has been determined. Of these, density is the most commonly used, and tables have been prepared for many common reagents, showing what percentage strength, in the case of each, corresponds to each given density.

22. What is the percentage strength of a solution prepared by dissolving 25 g. of sugar in 100 g. of water?

23. A solution of density 1.20 contains 27.3 per cent H_2SO_4. What is the total weight of one liter of such a solution, and what weight of H_2SO_4 does it contain?

24. A solution of density 1.27 contains 310 g. of NaOH in one liter. What is its percentage strength?

When two different liquids have very nearly the same density, then on mixing them there is obtained a mixture having an intermediate density that is very easily calculated. Thus, if 200 cc. of water (density, 1.00) are mixed with 100 cc. of any aqueous solution of density 1.06, then the total weight of the mixture will be $(200\times1.00)+(100\times1.06)=306$ g.; and its density will be $306\div300=1.02$. If the two liquids are very different in density, this method may give only very rough results, for a very considerable increase or decrease in volume may then take place when the two are mixed. Thus, 100 cc. of water (density, 1.00) when mixed with 100 cc. of sulfuric acid (density, 1.80) gives 192 cc. of solution, there being a contraction of 8 cc.

25. What is the actual density of the mixture just mentioned? What would have been its density if no contraction had taken place?

Problems involving the densities and percentage strengths of solutions involve no new principle. In any case,

$$\textbf{Volume}\ (\text{cc.})\times\textbf{density}\ (\text{g./cc.})\times\frac{\textbf{percentage strength}}{100}=\textbf{total}$$

weight of specified dissolved substance.

26. What weight of sodium hydroxide is contained in 50 cc. of a solution of density 1.10, containing 8.8 per cent NaOH?

27. How may the density of a solution be found from its percentage strength and the total weight of the specified dissolved substance in one liter of solution?

28. How many moles of sodium hydroxide in one liter of a solution of density 1.10, containing 8.8 per cent NaOH?

29. How many moles, and what weight of HCl will the preceding NaOH solution neutralize? What volume of solution, of density 1.20, containing 39.1 per cent HCl, will be needed to furnish this weight of HCl?

30. What weight of Na_2CO_3 is needed to neutralize 100 cc. of a solution of density 1.02, containing 14 per cent $HC_2H_2O_2$?

31. What volume of solution, of density 1.10, containing 17.1 per cent HNO_3, is needed to furnish 2 moles of HNO_3?

32. What weight of a 10 per cent solution of NaOH is needed to neutralize 100 g. of a 4 per cent solution of HCl?

33. How many cubic centimeters of a solution of density 1.20, containing 39.11 per cent HCl, will be required to react with 25 g. of calcium carbonate?

147.— Problems Involving Other Units than the Gram (for Weights) and Liter (for Volumes of Gases).—We have already noted that, as long as the quantities needed in a calculation are all weights or all volumes (of gases), the unit of weight or volume may be anything we please. However, if one of the quantities concerned is a **weight** and one a **volume of gas,** we need to be careful in the choice of units. We have seen that whenever weights are expressed in grams, volumes of gases are to be expressed in liters, each mole being equivalent to 22.4 liters of gas, at standard conditions.

But 1 gram = 1000 mg.;
= 1/1000 kg.;
= 0.0353 oz.;
while 1 l. = 1000 cc.;
= 1/1000 cu. m.;
= 0.0353 cu. ft.

Accordingly,

Whenever weights are expressed in—	***Volumes of gases should be expressed in—***
milligrams	**cubic centimeters**
grams	**liters**
kilograms	**cubic meters**
ounces	**cubic feet**

The methods to be applied in solving problems involving other units of weight than the gram and other units of volume than the liter are therefore the same as those we have already considered. One **ounce-molecule of gas is as many ounces as there are units in its molecular weight**; and occupies 22.4 **cu. ft.** A **milligram-molecule** occupies 22.4 **cc.**; a **kilogram-molecule, 22.4 cu. m.**

What volume of carbon dioxide gas can be obtained by fermenting 5 lbs. of glucose?

The weight is here given in the English system, and may be converted to *ounces*. The volume of gas will then be in *cubic feet.**

$$\begin{array}{lll} 5\times 16=80 \text{ oz.} & & ? \text{ cu. ft.} \\ C_6H_{12}O_6 & =2C_2H_5OH+ & 2CO_2. \end{array}$$

One ounce molecule = 180 oz. produces 44.8 cu. ft.
Thus, 80 oz. will produce

$$80/180\times 44.8=19.9 \text{ cu. ft., } \textit{Ans.}$$

Twenty-five cubic centimeters of CO_2 gas were obtained by fermentation. To what weight of glucose does this correspond?

The volume of gas is here given in *cubic centimeters*, hence the weight of glucose must be in *milligrams*.

$$\begin{array}{ll} ? \text{ mg.} & 25 \text{ cc.} \\ C_6H_{12}O_6=2C_2H_5OH & +2CO_2. \\ 180 \text{ mg. . . . produce . . .} & 44.8 \text{ cc.} \end{array}$$

To produce 25 cc will require

$$25/44.8\times 180=100.4 \text{ mg., } \textit{Ans.}$$

What volume of sulfur dioxide is obtained by burning 200 kg. of an ore having the formula $CuFeS_2$?

With the weight of ore in *kilograms*, the volume of gas must be in *cubic meters.*

$$\begin{array}{lll} 200 \text{ kg.} & & ? \text{ cu. m.} \\ 4CuFeS_2 & +13O_2=4CuO+2Fe_2O_3+ & 8SO_2. \\ 4\times(63.57+55.84+64.12) & & \\ =734.12 \text{ kg. . . .} & \text{produce . . .} & 8\times 22.4=179.2 \text{ cu. m.} \end{array}$$

Then 200 kg. will produce $200/734.12\times 179.2=48.9$ cu. m., *Ans.*

34. How many milligrams of carbon are contained in 33.6 cc. of acetylene, C_2H_2?

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* We get the same result, of course, if we leave the weight in pounds and say that every pound-molecule of gas occupies 16×22.4 cu. ft.

148.—Gram-Equivalent and Milligram-Equivalent.—Chemical calculations are often carried out in terms of a unit called the **gram-equivalent** (abbreviated g.-eq.). The meaning of this term depends on the type of chemical reaction concerned.

(1) In **neutralization** a gram-equivalent is the weight in grams corresponding to 1.008 g. of *replaceable hydrogen.*

For HCl it is one mole (36.468 g.); for H_2SO_4 half a mole; for H_3PO_4 one-third of a mole (providing all three of the hydrogen atoms of the acid are actually replaced in the given reaction).

Similarly for $NaOH$ one g.-eq. is one mole (40.008 g.); and for $Ca(OH)_2$, half a mole.

(2) In **double decomposition** a gram-equivalent is the weight in grams corresponding to one unit of *valence of metal* (or metal and hydrogen).

For $NaCl$ it is one mole (58.46 g.); for Na_2CO_3 it is half a mole. For $CaHPO_4$ it is a third of a mole (if both Ca and H are exchanged with another element in the double decomposition); or half a mole (if only Ca is exchanged).

(3) In **oxidation and reduction,** a gram-equivalent is the weight in grams corresponding to one unit of *valence change.*

A gram-equivalent of $KMnO_4$ to be used in double decomposition, is a whole mole; but to be used as an oxidizing agent in an acid solution it is only a fifth of a mole, since the valence of manganese then decreases from 7 (in $KMnO_4$, § 121) to 2 (as in $MnSO_4$), a decrease of five units.

This example illustrates the fact that the number of grams contained in a gram-equivalent is often not defined until we specify the reaction in which the given substance is to be used.

By a **millgram-eqivalent** (abbreviated mg.-eq.) we mean as many *milligrams* as there are grams in a gram-equivalent.

A gram-equivalent of Na_2SO_4 is $\frac{1}{2}\times(46+32.07+64)=71.03$ g. Thus, a milligram-equivalent of this same substance is 71.03 mg.

149. Three Ways of Expressing the Concentration of a Solution.— By the **concentration** of a solution we mean the **amount of dissolved substance in a unit volume.** It is commonly expressed in—

grams per liter,
moles per liter,
gram-equivalents per liter.

A **molal** (or **molar**) solution is one containing one *mole* of dissolved substance in a liter. Thus, 98.086 g. of H_2SO_4 in a liter of solution makes a molar solution.

A **normal** solution is one containing one *gram-equivalent* of dissolved substance in a liter. For H_2SO_4 this would be $\frac{1}{2}\times 98.086$ g. in 1 l. of solution; or the full 98.086 grams in 2 l. Since each liter of a normal solution contains one gram-equivalent, **each cubic centimeter of a normal solution contains one milligram-equivalent.** This statement is very important. The **normality** of a solution means its concentration, expressed as so many times that of a normal solution. Note the customary abbreviations of various normalities: N means normal; 2N, twice normal; N/2, half normal; N/10, one-tenth normal; 0.8654N, a solution having a concentration 0.8654 times that of a normal solution.

Distinguish carefully between 2N and N/2.

35. What is the normality of a solution of calcium chloride, containing 11.1 g. in a liter? How many times molar is such a solution?

36. What is the normality of an acid solution prepared by dissolving one mole of crystallized oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, in water and diluting to 5 l.?

37. What weight of anhydrous sodium sulfate is contained in 50 cc. of a molar solution?

150.—The Practical Advantage of Solutions of Known Normality.

—By working with solutions of known normality we are able to simplify many chemical calculations enormously. The number of cubic centimeters of a solution, multiplied by its normality, gives the number of milligram-equivalents of dissolved substance (**cc.×normality = mg.-eq.**). Furthermore, **a given number of milligram-equivalents of one substance will react with exactly the same number of milligram-equivalents of any other substance.***

Thus, 50 cc. of N/10 acid contains $50\times 1/10 = 5$ mg.-eq. This will react with 5 mg.-eq. of any base; i.e., with 5 cc. of N base solution, 50 cc. of N/10 solution; 100 cc. of N/20 solution, etc. Notice that **if we know the volume and normality of a solution we need not know the molecular weight nor even the formula of the dissolved substance.**

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* Provided, of course, that the milligram-equivalent is defined in both cases in the same way. One milligram-equivalent of a substance, defined with respect to oxidation, would not necessarily react with one milligram-equivalent of another, defined with respect to neutralization or precipitation.

38. What volume of a N solution of sodium hydroxide is needed to neutralize 75 cc. of N/10 citric acid?

39. What volume of N/5 barium hydroxide solution is needed to completely precipitate 100 cc. of a N solution of any magnesium salt?

40. Ten cc. of a N solution of potassium iodide are mixed with 19 cc. of a N/2 solution of silver nitrate. Which substance was used in excess? Express this excess as a fraction of a milligram-equivalent. As a fraction of a mole.

151. Problems Involving Normal Solutions.—The method for solving problems involving normal solutions may best be explained by a few examples.

What weight of sodium chloride is needed to react with 25.7 cc. of N/10 *silver nitrate solution?*

The 25.7 cc. of N/10 $AgNO_3$ solution is 2.57 cc. of N solution, and contains 2.57 mg.-eq. (§ 148) of $AgNO_3$.

This will react with 2.57 mg.-eq. of NaCl.

But 1 mg.-eq. of $NaCl = \frac{\text{mol. wt. in mgs.}}{\text{valence of Na}} = \frac{58.46}{1} = 58.4$ mg.

The total weight of NaCl is therefore $2.57 \times 58.46 = 150.24$ mg., *Ans.*

When 25 cc. of sulfuric acid are precipitated by a barium salt, 1.527 g. of $BaSO_4$, are produced. Calculate the normality of the acid.

The 25 cc. of acid of normality x are equivalent to 25 x cc. of normal acid, or 25 x mg.-eq. of H_2SO_4.

This will produce 25 x mg.-eq. of $BaSO_4$.

But 1 mg.-eq. of $BaSO_4 = \frac{\text{mol. wt. in mgs.}}{\text{valence of Ba}} = \frac{233.42}{2} = 116.71$ mg.

The 25 x mg.-eq. of $BaSO_4$ are therefore $25\,x \times 116.71$ mg.; this must be equal to the stated weight of $BaSO_4$, 1527 mg.; i.e.,

$$25\,x \times 116.71 = 1527;$$

whence $x = 0.5233$ N., *Ans.*

What volume of N/5 *hydrochloric acid is needed to react with 1.06 g. of Na_2CO_3 (mol. wt. 106)?*

The 1.06 g. is 1/100 of a mole or 1/50 of a gram-equivalent. It will therefore require 1/50 of a gram-equivalent of HCl to react with it. This is 1/50 of a liter of N HCl; or 20 cc. of N HCl; or 100 cc. of N/5 HCl, *Ans.*

What is the normality of an alkaline solution, 25 cc. of which neutralize 26.42 cc. of N/2 *acid?*

Since less alkali is needed than acid, the alkali must be somewhat the more concentrated; plainly

$$\frac{26.42}{25} \times \tfrac{1}{2}\text{N} = 0.5284 \text{ N, } \textit{Ans.}$$

EXERCISES

1–40. Review the problems and exercises of this chapter.

41. Balance the formulation:

$$C_2H_2+O_2 \rightarrow CO_2+H_2O.$$

42. What volumes of each of the other gases are consumed or produced when 2.74 cc. of acetylene (C_2H_2) are burned?

43. What volume of acetylene gas must be burned to produce 11 g. of carbon dioxide?

44. How many cubic feet of acetylene gas are needed for every pound of water vapor produced?

45. What weight of carbon is contained in 100 cu. ft. of acetylene?

46. How many milligrams of carbon are contained in 11.2 cc. of acetylene?

47. What approximate volume of *air* is needed to burn 44.8 cu. ft. of acetylene? (Air is about one-fifth oxygen by volume.)

48. Concentrated hydrochloric acid has a specific gravity of 1.2 and contains 40 per cent HCl by weight. How many liters of hydrogen chloride gas, at standard conditions, are required to prepare one liter of concentrated hydrochloric acid?

49. If a solution of concentrated hydrochloric acid has a specific gravity of 1.20, and contains 40 per cent HCl by weight, what weight of common salt will be required, for every liter of concentrated hydrochloric acid produced, in the reaction of the first half of § 177?

50. How many milligram-equivalents of sodium sulfate, Na_2SO_4, in 0.2 g. of that material?

51. What volume of normal hydrochloric acid is needed to decompose 1 g. of anhydrous sodium sulfite, to liberate sulfur dioxide gas?

52. What volume of sulfur dioxide gas, at standard conditions, is liberated in the preceding problem?

53. What approximate weight of nitrogen can be contained in a cylinder of 20 liters capacity, under a pressure of 20 atmospheres?

54. What volume of a solution of sulfuric acid, of specific gravity 1.25, containing 33.4 per cent H_2SO_4, will be needed to prepare 10 liters of N/5 solution?

55. What is the normality of an acid, 27.4 cc. of which are required to react with 265 mg. of anhydrous sodium carbonate, liberating carbon dioxide

CHAPTER XII

HOW CHEMICAL FORMULAS ARE DERIVED

In preceding chapters we have already made extensive use of atomic weights and chemical formulas, without discussing the question of how we get them—beyond remarking that they are based on actual determinations of the proportions by weight in which elements combine (§ 37). The reasoning that is involved is not really very difficult, if we take care to note the *order* in which the several steps are developed (follow the diagram in § 164).

152. Recalculation of Gas Volumes to New Conditions.—Review § 20. Whenever a gas is measured under ordinary laboratory conditions, its volume must be recalculated to standard conditions before it is possible to determine how many moles are represented. One or two examples will make the method clear.

A gas occupies 25.45 cc. at 20° C. and 740 mm. pressure. Required its volume at 0° C. and 760 mm. pressure.

Original conditions: $V_1 = 25.45.$ $P_1 = 740.$ $T_1 = 293°$ A.
Final conditions: $V_2 = ?$ $P_2 = 760.$ $T_2 = 273°$ A.

Notice, first, that the gas is cooled from 20° C. to 0° C. or from 293° A. to 273° A. It will plainly *contract* and occupy a *smaller* volume than before. The original volume must therefore be multiplied by a fraction *smaller* than one, evidently 273/293.

Again, when the pressure is increased from 740 to 760 the gas will be *compressed*, and will occupy a smaller volume than before; the preceding volume must therefore be multiplied by another fraction smaller than one, namely, 740/760. For the final volume we have then:

$$V_2 = 25.45 \times \frac{273}{293} \times \frac{740}{760} = 23.10 \text{ cc.}$$

Ten cubic feet of air measured at 95° F., under a pressure of 80 lbs. per sq. in. will occupy what volume at 41° F., under a pressure of 35 lbs. per sq. in.?

Original conditions: $V_1=10.$ $P_1=80.$ $T_1=308°$ A.
Final conditions: $V_2=?$ $P_2=35.$ $T_2=278°$ A.

Nothing different in principle is introduced by expressing the volume in cubic feet and the pressure in pounds per square inch. We note, first, that 95° F. = 35° C., = 308° A.; and that 41° F. = 5° C. = 278° A. (§ 19). The air is *cooled* from 308° A. to 278° A., which results in a *smaller* volume. The original volume must therefore be multiplied by a fraction *smaller* than one, evidently 278/308. Then the pressure is decreased from 80 to 35 lbs. per sq. in., and the gas expands, occupying a *larger* volume than before. We must therefore multiply by another fraction, this time *larger* than one, evidently 80/35. The final volume is then:

$$V_2=10\times\frac{278}{308}\times\frac{80}{35}=20.63 \text{ cu. ft.}$$

153. Vapor Density.— The **vapor density** of a substance is usually expressed as **the weight, in grams, of one liter of the vapor.** Thus, the vapor density of water, recalculated to standard conditions, is 0.804 g. per liter. The vapor density of a volatile substance, such as chloroform, is sometimes determined by filling a small bulb of known capacity with the vapor, and weighing this directly.

More commonly, a known weight of the substance is dropped to the bottom of a long bulb, which is surrounded with a heated jacket of constant temperature (**Victor Meyer Method**). If conditions are right, the substance vaporizes within a few seconds, and the vapors produced expel an equal volume of air from the upper portion of the apparatus. By collecting this air over water, and recalculating its volume to standard conditions, we obtain the volume which the given weight of vapor would itself have occupied, if uncondensed under standard conditions. From this the vapor density may be calculated.

1. In one such experiment, 0.1200 g. of a substance furnished 24.5 cc. of air, at 27°, under a pressure of 740 mm., corrected for the vapor pressure of water. Calculate the vapor density of the substance.

154. Molecular Weights from Vapor Densities.—Review § 139. Since the vapor density of a substance, recalculated to standard conditions, gives the weight of one liter under these conditions, we need only multiply by 22.4 to obtain the weight in grams corresponding to one mole. Otherwise expressed, **the molecular weight of any volatile substance is the number expressing the weight in grams of 22.4 l. of the substance, recalculated to standard conditions, in the condition of a gas or vapor.** Molecular weights thus obtained are usually only **approximate,** because the recalculation of volumes to standard conditions is usually based on laws that are only roughly true (§ 20). A mole of a gas or vapor is not exactly 22.4 liters, at standard conditions. Nevertheless, by taking account of the deviation of any given gas from the behavior expressed by the ideal gas laws, vapor density measurements may be made to give **exact molecular weights.**

2. What is the approximate molecular weight of a substance, if 0.105 g. of its vapor occupy 100 cc., at 20° C., under a pressure of 740 mm. (corrected for the vapor pressure of water)?

3. From the formula of ammonia, calculate its exact molecular weight, and *theoretical density*. Explain why the actual density of ammonia may be slightly different from the theoretical density.

155. Relative Density.—By Avogadro's Principle (§ 22) equal numbers of molecules occupy equal volumes. Thus, the relative weights of equal volumes (relative densities) may be determined by comparing molecular weights. For example, hydrogen sulfide (mol. wt., 34) has very nearly twice the density of ammonia (mol. wt., 17).

4. Which is the heavier, and in about what proportion, hydrogen chloride or chlorine?

5. Is water vapor heavier or lighter than nitrogen?

The weight of 22.4 liters of dry air, at standard conditions, is very nearly 29 g. The average molecular weight of the gases of the atmosphere is accordingly about 29; and **the relative density of any gas, as compared with air, may be found by dividing its molecular weight by 29.** Thus, carbon dioxide (mol. wt., 44) is $44 \div 29 = 1.5$ times as heavy as air.

6. Which of the following gases and vapors are lighter than air, and which heavier, and in about what proportion? Hydrogen, oxygen, nitrogen, water vapor, bromine (Br_2).

156. Association and Dissociation.—But, though the vapor density method will give the molecular weight of a substance in the condition of a gas or vapor, its molecular weight when condensed to liquid is sometimes *very much greater*; for during the process of liquefaction the simple molecules that exist in gases may join together in groups or clusters. Thus, water, which in the condition of vapor has the molecular weight 18, corresponding to the formula H_2O, in the liquid condition is believed to consist for the most part of molecules of twice or three times that weight, corresponding to the formulas $(H_2O)_2$ and $(H_2O)_3$. **A union of simple molecules, all of the same kind, to form more complex molecules, is called *association*.**

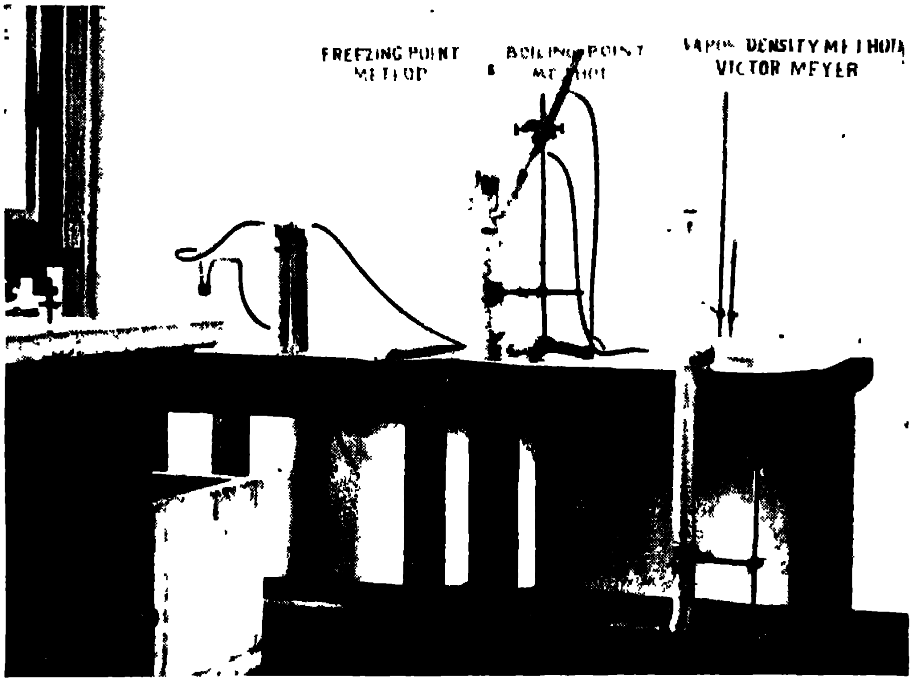

Fig. 42.—A physical chemistry laboratory. Apparatus for determining molecular weights, by vapor density, freezing point, and boiling point methods.

The reverse process is **dissociation** (§ 102)—**the breaking up of complex molecules into others of lower molecular weight**—not necessarily alike. An example is the partial dissociation of ammonium chloride, at high temperatures, into hydrochloric acid and ammonia gas:

$$NH_4Cl \rightleftarrows HCl + NH_3.$$

In this dissociation, one molecule becomes two. But an increased number of molecules, by Avogadro's principle (§ 22) means a correspondingly increased volume. Accordingly, **whenever a gas dissociates on being heated, it expands more rapidly with increasing temperature than the Law of Charles would indicate.**

7. Twenty per cent of the molecules of ammonium chloride are dissociated at a certain temperature. What will be the *average molecular weight* for the three kinds of molecules then present?

157. Molecular Weights of Substances in Solution.—(Review §§ 99, 100.) If a substance is not a gas and not easily vaporized, it is impossible to get its molecular weight by the method described in § 154. But if it happens to be *soluble*, its molecular weight in solution may be determined by a determination of the freezing point, boiling point, or osmotic pressure of the solution, in comparison with that of the pure solvent. **One mole of any soluble substance—not an acid, base, or salt—dissolved in a given weight of solvent, produces very nearly the same effect on vapor pressure, boiling point, freezing point, or osmotic pressure as is produced by one mole of any other.**

Thus, one gram-molecule (or mole) of cane sugar, $C_{12}H_{22}O_{11}$, namely, 342 g., dissolved in 1 l. of water, gives a solution which begins to freeze at $-1.86°$ C. One gram-molecule of ethyl alcohol, C_2H_5OH, is only $24+6+16=46$ g., but has the same effect on the freezing point of a liter of water as the 342 g. of sugar.

A mole of almost any soluble substance—not an acid, base, or salt—dissolved in 1000 cc. of water, forms a solution freezing at $-1.86°$ C. Accordingly, **to determine the gram-molecular weight of a soluble substance, find what weight needs to be dissolved in a liter of water to give a solution freezing at $-1.86°$ C.** Similar statements apply to molecular weights from freezing-point determinations of solutions in other solvents than water; or from determinations of boiling points or osmotic pressures. **But acids, bases, and salts have a greater effect than other substances on freezing points, boiling points, etc.,** because they are ionized. (Read § 256.)

Five grams of a substance, dissolved in 75 cc. of water, forms a solution freezing at $-0.363°$ C. Calculate its molecular weight.

Five grams in 75 cc. is the same as (1000/75)×5=66.67 g. in 1 l. This gives a lowering of 0.363°. To give the standard *molecular lowering*, 1.86°, the amount dissolved in a liter would need to be *proportionately greater*:

$$\frac{1.86}{0.363}\times 66.67=342.^{*}$$

The approximate molecular weight is therefore 342.

8. What will be the approximate freezing point of a solution containing 0.46 g. of ethyl alcohol in 50 cc.?

158. Approximate Atomic Weights. We have just seen that the **approximate molecular weights** of a great many substances may easily be determined—for gases or vapors by finding the weight in grams of 22.4 l., recalculated to standard conditions; and for soluble substances most easily by seeing how many grams need to be dissolved in 1000 g. of water to lower the freezing point 1.86° C.

But as soon as we know the approximate molecular weights of a great many compounds of known percentage composition it is easy to get the **approximate atomic weights** of the elements that these compounds contain. An example will make the method clear.

Chloroform vapor, recalculated to standard conditions, has a density of about 5.3 g. per liter. Thus, its molecular weight is approximately 22.4×5.3 =118.7. But chloroform is known to contain 10.05 per cent C, 0.85 per cent H, and 89.10 per cent Cl. Accordingly, one gram-molecule contains, roughly:

10.05 per cent×118.7=11.9 g. of carbon,
0.85 per cent×118.7=1 g. of hydrogen,
89.10 per cent×118.7=105.7 g. of chlorine.

We do the same thing with a great many other compounds of carbon, determining in each case the *number of grams of each element in one gram-molecule of the compound.* It has been proved that no compound contains less carbon in a gram-molecule than does chloroform. Thus it seems probable that chloroform contains *the least possible amount of carbon in a molecule*; in other words, *one atom.*

Similarly, for hydrogen. No other compound of hydrogen contains less hydrogen in one gram-molecule than does chloroform. Accordingly we assume that chloroform contains the least possible amount of hydrogen in a molecule; in other words, one atom.

But the least amount of chlorine in one gram-molecule of any chlorine compound is about one-third that found in one gram-molecule of chloroform.

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* Such problems may be solved by proportion, if that seems easier.

The formula of chloroform must accordingly be $CHCl_3$; and the atomic weights of the three elements concerned must be, approximately:

$$C = 11.9, \quad H = 1, \quad Cl = \tfrac{1}{3} \times 105.7 = 35.2.$$

These are only *approximate atomic weights*, however, for they were derived from molecular weights that are determined only approximately by the methods we have described.

To summarize: **The atomic weight of any element is *approximately* the number expressing the least weight of that element, in grams, in one-gram-molecule of any of its compounds.**

9. Complete the following table, and state what additional assumption must be made before any conclusion can be drawn regarding the atomic weight of carbon:

Substance	*Mol. Wt.*	*%C.*	*Wt. of C in 1 Mole*
Carbon monoxide	28	42.9	
Ethylene	28	85.7	
Propane	44	81.8	
Butane	58	82.8	

10. Among the different gaseous compounds of bromine, none contains less than about 3.8 g. of bromine in a liter, at standard conditions. What conclusion may be drawn?

159. Two Checks on Approximate Atomic Weights.—The reader should now refer to the graphical summary at the end of this chapter (§ 164) to review the steps by which we have advanced. Beginning with the atomic and molecular theories, and by reasoning from vapor densities or freezing points, we first derived **approximate molecular weights.** From these, by taking note of the least weight of each element in one molecule of any of its compounds, we derived a set of **approximate atomic weights.** From these in turn we shall presently derive **exact atomic weights** and **formulas.**

But all our chemical formulas depend on the accuracy of our reasoning, and a chain is no stronger than its weakest link. It is therefore important that we look for independent confirmation of our approximate atomic weights, before proceeding. Two such confirmations do indeed exist:

(1) **If we list the elements in the order of increasing atomic weights,** determined approximately as just described, **we find that**

elements of similar properties occur at regular intervals. Thus

the 2d element is like the 10th and 18th;
the 3d element is like the 11th and 19th;
the 4th element is like the 12th and 20th;

and so forth. This is the **Periodic Law,** discussed in detail hereafter (§§ 165–173). The regular variation of properties, which is shown when the elements are arranged in the order of increasing atomic weights, is taken as good evidence that these atomic weights are at least approximately correct.

(2) **The approximate atomic weight of a solid element multiplied by its specific heat,* is almost always about 6**—closely enough to prevent the approximate atomic weight from being taken at half or twice its true value. This is the **Law of Dulong and Petit.** Thus, any doubt about the atomic weight of sulfur being approximately 32 must disappear as soon as experiment has shown that the specific heat of sulfur is 0.17; for $0.17 \times 32 = 5.44$. This is close enough to 6 to show that the true atomic weight of sulfur cannot differ from our approximate result by more than a few per cent.

11. From its atomic weight, estimate the number of calories that would be needed to heat 1 kg. of lead from the freezing point to the boiling point of water.

12. Which will melt the greater quantity of ice, a pound of iron, or a pound of lead, if both are previously heated to the same temperature? Explain.

160. The Three Things Needed to Derive a Chemical Formula. – To derive the formula of a compound it is necessary to know (1) **its molecular weight** (determined by one of the methods just described); (2) **the percentage of each element in it** (as determined by analysis); and (3) **the atomic weights of all these elements.**

Thus, from the data given in § 158, it was easy to see that the formula of chloroform must be $CHCl_3$.

Again, camphor is known to have a molecular weight of about 152. It contains 78.9 per cent carbon, 10.6 per cent hydrogen, and 10.5 per cent oxygen. A molecule accordingly contains about—

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* By the specific heat we mean the number of calories (Appendix H) of heat needed to raise the temperature of 1 g. of the substance 1° C. The specific heat of water is accordingly 1—varying slightly with the temperature.

78.9 per cent × 152 = 120 parts by weight of carbon;

10.6 per cent × 152 = 16.1 parts by weight of hydrogen;

and

10.5 per cent × 152 = 16 parts by weight of oxygen.

Comparing these numbers with the atomic weights of the three elements (C = 12.005; H = 1.008; O = 16), it is evident that camphor has the formula $C_{10}H_{16}O$.

If the substance for which the formula is to be derived is both non-volatile and insoluble, its molecular weight is always unknown. The most that we can then do is to find the simplest of many possible formulas.

Thus, quartz contains 46.93 per cent silicon, and 53.07 per cent oxygen; namely, 46.93 g. and 53.07 g. in a total of 100 g. Dividing these figures by the respective atomic weights we get:

$$\begin{aligned} 46.93 \div 28.3 &= 1.66 \text{ gram-atoms of silicon;} \\ 53.07 \div 16. &= 3.32 \text{ gram-atoms of oxygen.} \end{aligned}$$

But 3.32 is just twice 1.66. The simplest possible formula, or *empirical formula*, for quartz is thus SiO_2; though the true formula, if the substance were volatile or soluble, might prove to be Si_2O_4, Si_3O_6, or any other whole multiple of the empirical formula.

13. A certain compound contains 26.19 per cent nitrogen, 66.28 per cent chlorine, and 7.53 per cent hydrogen. Calculate its simplest possible (or empirical) formula. What are some of the other formulas which this substance may possibly have?

14. What classes of compounds are of undetermined molecular weights? Give several examples.

161. Formulas of the Elements.—The formulas of **elements** are derived in the same way as those of compounds. Thus **the *least* weight of oxygen contained in a given volume of any gaseous compound is just *half* the weight of oxygen in the same volume of pure oxygen gas.** Accordingly the least possible weight of oxygen in a molecule of any compound (i. e., one atom of oxygen) must be half the weight of a molecule of oxygen gas; and a molecule of oxygen must contain two atoms. If we represent the atom by O, the molecule must be O_2.

By a similar reasoning we may show that chlorine is Cl_2, hydrogen is H_2, nitrogen is N_2, etc. But sulfur vapor may be S_8 (at about 193° C.) or S_2 (at 800° C.). The inert gases (§ 583) and the vapors of most metals have but one atom in a molecule—He, Ne, A, Hg, Zn, etc.

162. Exact Atomic Weights.—Since the principle of Avogadro is only roughly true, molecular weights derived from the relative densities of gaseous compounds are but approximate ones, and lead only to **approximate atomic weights.** The same is true of freezing-point determinations.

But when we have determined both the approximate atomic weight of an element and its combining weight,* we are in a position to derive its exact atomic weight, for the exact atomic weight of an element is always simply related to its combining weight (review § 37).

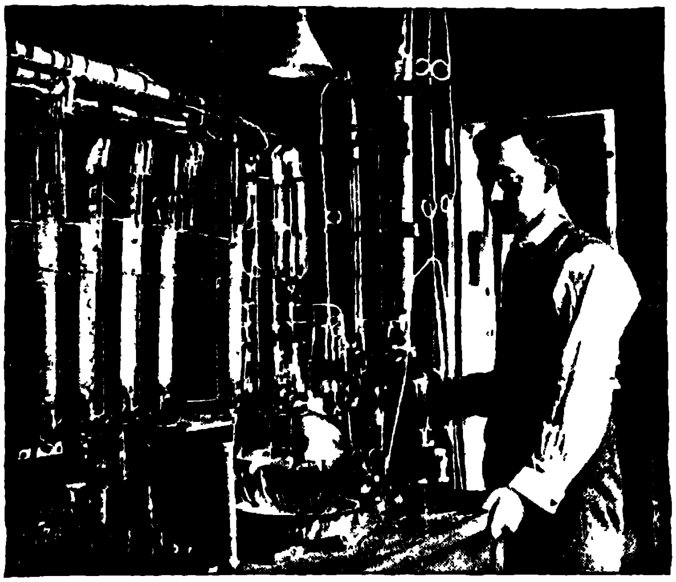

FIG. 43.—Research in Physical Chemistry. Harvard University. Determination of the atomic weight of radioactive lead.

Thus, the approximate atomic weight of phosphorus—the least weight of that element in 22.4 liters of any of its gaseous compounds—is about 30. Its combining weight the weight of phosphorus combined with 8 parts of oxygen to form phosphorus pentoxide—is 6.208. Now, 30 is evidently about five times 6.208; accordingly, the exact atomic weight is exactly $5 \times 6.208 = 31.04$.

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* Usually defined, somewhat arbitrarily, as the weight of a given element which will combine with or replace 8 g. of oxygen. A given element may have several different combining weights, since it may combine with oxygen in more than one proportion.

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15. The specific heat of a solid element is 0.112. Its combining weight is 18.61. What is its exact atomic weight?

To summarize: **The exact atomic weight of an element is the simple multiple or sub-multiple of its combining weight that comes nearest to its approximate atomic weight, already determined.**

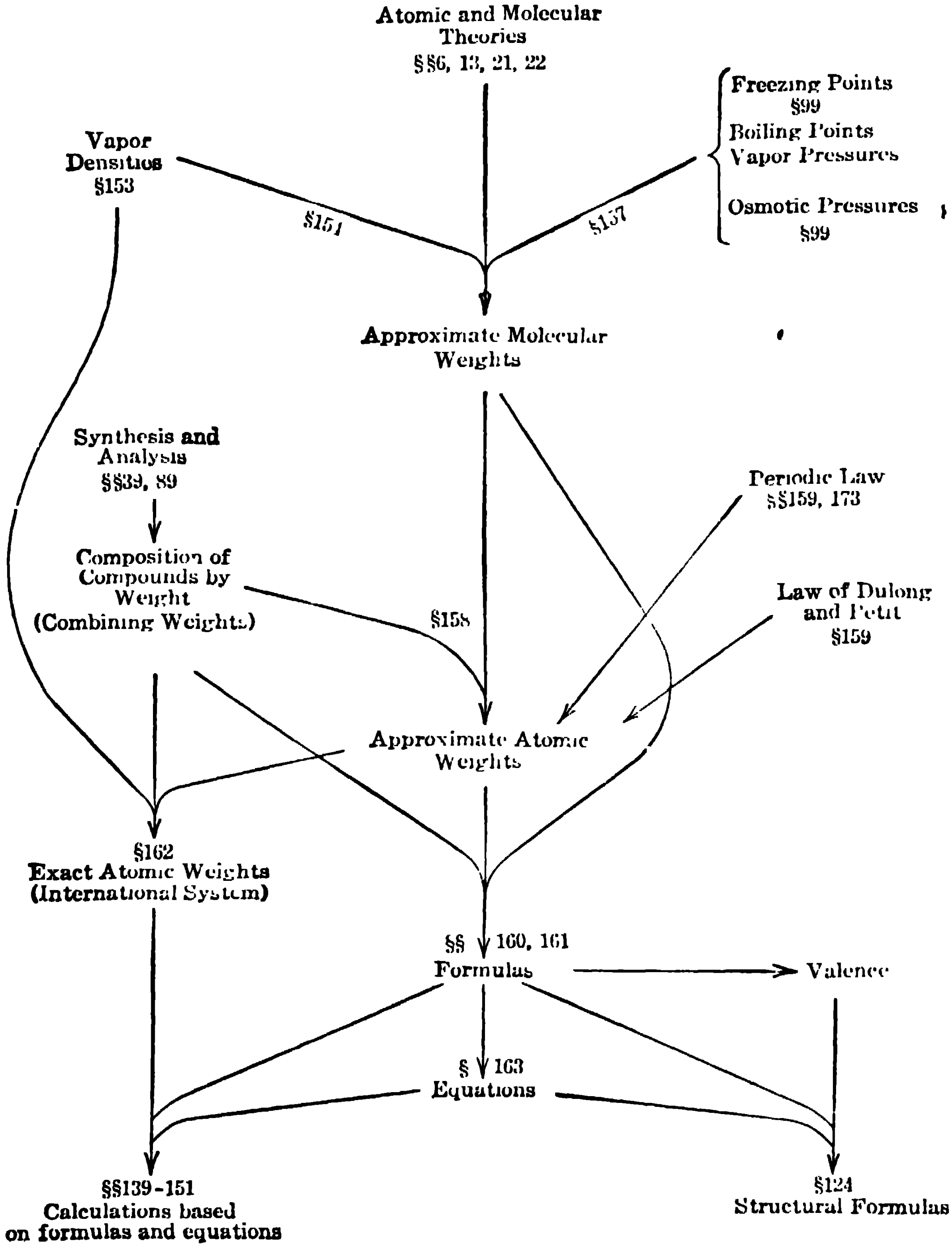
The accurate determination of the combining weights of the elements, and thus indirectly of their exact atomic weights, has been the subject of an immense amount of labor. Many chemists have given years of their lives to such investigations, which call for a thorough knowledge of chemical principles and the properties of chemical compounds, combined with the highest experimental skill, and unlimited patience. The results that are being obtained to-day are reviewed each year by a committee of eminent chemists representing the United States, England, France, Germany, and Switzerland. The data that appear most reliable are then published as an *International Table of Atomic Weights* (front cover).

163. The History of a Chemical Equation.—Before an equation can be written, experiments must be performed to separate and identify the various products of the reaction. This often calls for a very high order of ingenuity, experimental skill, and patience. But even after the products of the reaction have thus been separated, identified, and weighed, the equation cannot be written until their formulas are known. We have just seen (§ 161) that these call for a determination of individual molecular weights and percentage compositions, and involve the use of atomic weights that are the result of the accumulated labor and thought of many investigators, during several generations. Thus, even so simple an equation as that representing the decomposition of potassium chlorate by heat,

$$2KClO_3 \rightarrow 2KCl + 3O_2,$$

is the product of an unbelievable amount of toil and pains.

164. Graphical Summary.—



EXERCISES

16. Review the topics listed in the graphical summary, paying particular attention to portions of the text printed in black type. Then reproduce the summary from memory, stating briefly, in words, the successive stages of reasoning there represented by arrows.

17. How many grams of sulfur in one mole of sulfur dioxide?

18. From the formula of ammonia, NH_3, calculate the weight of 1 liter of that gas, at standard conditions.

19. What volume of ethylene gas, C_2H_4, at standard conditions, weighs 140 g.?

20. Write an equation to express the fact that nitrogen tetroxide, N_2O_4, when heated, partially dissociates, to form molecules of half the molecular weight here indicated.

21. What is the approximate freezing point of a solution containing 6.2 g. of glycol, $C_2H_4\ (OH)_2$, in 1 liter of water?

22. If glycerol, $C_3H_5(OH)_3$, and alcohol, C_2H_5OH, sold for the same price per pound, which would be the more effective as an "anti-freeze" in automobile radiators? Why?

23. Explain how the approximate atomic weight of an element is determined. Why is it only approximate?

24. The specific heat of a certain element, *X*, is 0.0305. In one of its oxides 51.8 g. of *X* are combined with 8 g. of oxygen. What is its exact atomic weight?

25. A certain element is known to be intermediate in properties between chromium (Cr) and iron (Fe). Consult the periodic table to determine its approximate specific heat.

26. If a compound of chlorine were to be discovered containing just half the weight of chlorine in a given volume that is contained in hydrogen chloride gas, what change would need to be made in the atomic weight of chlorine? How would this affect the formulas of all compounds containing chlorine?

27. From the formula of carbon bisulfide, find the approximate weight of 1 liter of its vapor, recalculated to standard conditions

28. From the formula of potassium dichromate, calculate its percentage composition.

29 A certain compound contains 1.26 per cent hydrogen, 38.78 per cent phosphorus, and the rest oxygen. Calculate its simplest possible formula. What are some other possible formulas?

30. A certain compound contains 14.24 per cent iron, 9.20 per cent ammonium (NH_4), 16.33 per cent sulfur, 32.65 per cent oxygen, and the rest water of hydration. Calculate its simplest possible formula.

31. The vapor of a certain liquid is known to be about twice as heavy as air. What is its approximate molecular weight? If it contains 62.02 per cent carbon, 10.12 per cent hydrogen, and 27.56 per cent oxygen, what is its formula?

32. What weight of water vapor and what weight of carbon dioxide will result from the combustion of 1 g of the preceding compound?

33. To what particular class of elements does the law of Dulong and Petit apply? State the law, and explain its use.

34. If 350 mg. of a certain vapor occupy 90 cc., at 27° C., under a pressure of 800 mm. of mercury, what is the weight of 1 liter, in grams, recalculated to standard conditions? What is the approximate molecular weight of this substance?

35. Calculate the approximate weight of a liter of dry air, at standard conditions?

36. When the air in a flask of 500 cc. capacity is displaced by a certain gas, the increase in weight is 670 mg. What is the molecular weight of the gas?

37. Explain (§ 37) why the percentage composition of a single compound is insufficient to determine the atomic weights of the elements contained in it.

38. What classes of substances are of unknown molecular weights? Give several examples, not found in the text.

39. Explain just what data are needed in order to derive the formula of a compound. Illustrate the process for water.

40. Explain how it has been proved that the formula of chlorine is Cl_2.

41. What are combining weights? What combining weight has hydrogen, in water, and in hydrogen peroxide, respectively?

42. What data are needed to derive the exact atomic weight of an element. Illustrate the process, using imaginary figures for an element X.

43. What is the standard molar volume? Show how it is calculated for oxygen gas.

Problems Based on the Gas Laws

When a gas is collected over water, water vapor mingles with the gas and relieves the latter of a part of the pressure that it would otherwise have to bear. The effective pressure on the gas itself is thus *the total pressure less the vapor pressure of water at the given temperature.* The vapor pressure of water may be found in the chart in *Appendix A*, where the middle scale represents temperatures and the upper scale the corresponding vapor pressures.

Thus, at 20° C. the vapor pressure of water is 17.4 mm. (Check this.) Then if a gas is collected over water at 20° C., with the barometer standing at 740 mm. (and with the water standing at the same level within and without the vessel) the true pressure on the gas will be 740 − 17.4 = 722.6 mm.

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44. What is the vapor pressure of water at 15° C., and at 27° C., respectively?

45. What weight of water is shown by the chart to be contained in 1 liter of saturated air at 30° C. (lower scale)?

46. At what temperature does water boil (§ 86) when the external pressure is 50 mm.?

47. What is the volume, dry, at standard conditions, of a gas which measures 100 cc., when collected over water at 27° C., with the barometer standing at 756.5 mm.?

48. A certain gas measures 100 cc. when collected over water at 17° C. with the barometer standing at 730 mm. What will be its volume, dry, under the same conditions of temperature and pressure?

Part II

THE NON-METALS

CHAPTER XIII

THE PERIODIC LAW

165. Passing the Elements in Review.—Let us pass the elements before us in review, *in the order of increasing atomic weight:*

1. The element of lowest atomic weight is **hydrogen,** H = 1.008. This is a colorless gas, chemically like a metal, for it unites with non-metals, and is liberated at the cathode during electrolysis; but it is physically like a non-metal, for at low temperatures, hydrogen is a snow-white, non-conducting solid.

2. The element of next higher atomic weight is **helium,** He = 4. This is likewise a colorless gas, but certainly no close relative of hydrogen, for it is *chemically inert.* Exposed to the highest temperatures or to intense electrical discharges, or brought into contact with such active elements as fluorine or potassium, it fails to do anything at all.

3. Next comes **lithium,** Li = 6.94, a soft, silvery-gray, low-melting metal, so light that it floats on water like wood, and so active chemically that it decomposes water, to liberate hydrogen and form an active base, lithium hydroxide. Plainly, this element is no close relative of either hydrogen or helium.

4. The element of next higher atomic weight is **glucinum,** Gl = 9.1, likewise a metal, but not such an active one as lithium, and very much harder, heavier, and more difficult to melt. Unlike lithium, again, it shows a valence of two in all its compounds. Evidently this is a member of still a different family.

Thus we examine in succession:

5. **Boron,** B = 10.9, a solid, infusible non-metal, valence 3.

THE PERIODIC TABLE

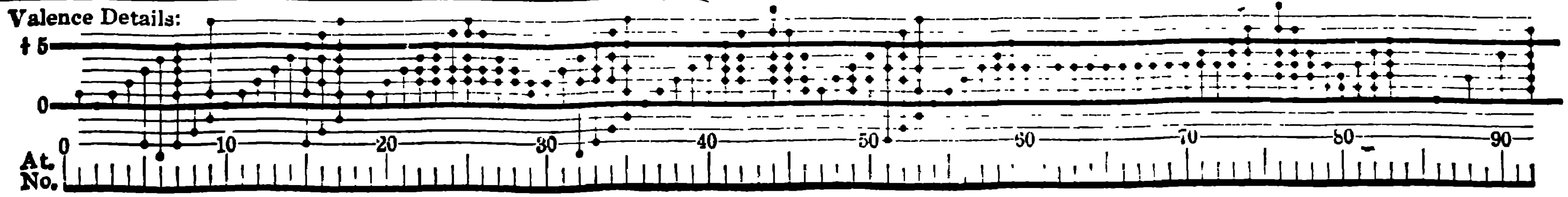
O	IA R_2O	IIA RO	IIIA R_2O_3	IVB RO_2	VB R_2O_5	VIB RO_3	VIIB R_2O_7				IB R_2O	IIB RO	IIIB R_2O_3	IVA RO_2	VA R_2O_5	VIA RO_3	VIIA R_2O_7
									1 H 1.008								
2 He 4.00	3 Li 6.94	4 Gl 9.1	5 B 10.9											6 C 12.005	7 N 14.008	8 O 16.000	9 F 19.0
10 Ne 20.2	11 Na 23.00	12 Mg 24.32	13 Al 27.0											14 Si 28.1	15 P 31.04	16 S 32.06	17 Cl 35.46
INERT GASES	LIGHT METALS								VIII Transition Group Valence Variable				HEAVY METALS			NON-METALS	
18 A 39.9	19 K 39.10	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96	34 Se 79.2	35 Br 79.92
36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Yt 89.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43 ? 99±	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92
54 Xe 130.2	55 Cs 132.81	56 Ba 137.37	57-72 Rare Earths 139-179		73 Ta 181.5	74 W 184.0	75 ? 188±	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.20	83 Bi 209	84 Po 210	85 ? 219±
86 Rn 222.4	87 ? 225±	88 Ra 226.0	89 Ac 230	90 Th 232.15	91 Pa 234.2	92 U 238.2											

Arrows indicate directions of increasing basic properties. Sloping lines indicate the degree of relationship between Extreme Groups (A) and Intermediate Groups (B), greatest for Group IV, decreasing in both directions, and nearly disappearing with Groups I and VII.

The rare earth elements are:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	?	Sa	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ct

Valence Details:



6. **Carbon,** C = 12.005, a solid, infusible non-metal, valence 4.

7. **Nitrogen,** N = 14.008, a gaseous, inactive non-metal, valence variable.

8. **Oxygen,** O = 16.000, a gaseous, active non-metal, valence −2.

9. **Fluorine,** F = 19.0, gaseous, extremely active, non-metal, valence −1.

Thus far we are impressed by the lack of similarity between the elements listed. There is hardly a single important point of resemblance. Plainly, **the nine elements of lowest atomic weights are members of nine different families.**

But hereafter resemblances appear. For,

10. **Neon,** Ne = 20.2, is a colorless gas, forming no compounds, and therefore of valence 0. Here at last is a relative of the second element, helium.

11. **Sodium,** Na = 23.00, is a soft, easily melting metal, floating on water, and decomposing it. Valence 1. Plainly a relative of the third element, lithium.

12. **Magnesium,** Mg = 24.32, a metal, so much like the fourth element, glucinum, that we might almost repeat our former description, word for word.

We should expect the thirteenth element, **aluminum,** to resemble the fifth, boron, at least in its valence—and it does; the next, **silicon,** to resemble the sixth, carbon, and it does. Thus it begins to appear that **if we arrange the elements in the order of increasing atomic weight, elements of similar properties appear at regular intervals.** This is a rough statement of the Periodic Law, previously referred to as a means of checking approximate atomic weights, derived by other methods (§ 159).

166. The Periodic Table.—The recurrence of similar elements at regular intervals makes it possible for us to arrange the elements in the order of increasing atomic weight, but in such a way as to bring related elements together in the same vertical column. The final result is shown in the table on the opposite page. Hydrogen is set out by itself, since it resembles no other element very closely. The eight following elements belong, as we have seen, to eight different families. We therefore set them down in the first horizontal row, four at the left (He, Li, Gl, and B) and four at the right (C, N, O, F).

In the second horizontal row, we set down the eight following elements, from neon (Ne) to chlorine (Cl) under the elements of the first row of most closely corresponding properties. These two rows are what we shall call the **two short periods.**

The third horizontal row begins with argon (A), which is a gas, similar in its chemical inertness to helium and neon; but before we find another element bromine (Br) that closely resembles chlorine and fluorine, we must pass over, not eight, but eighteen different elements. This is the **first long period.** The first four and the last four elements of this period resemble the corresponding members of the two preceding short periods.

A second long period, beginning with krypton (Kr), and ending with iodine (I) is beautifully regular; for each element is found to resemble the corresponding element of the preceding long period, and is accordingly placed under the latter. There is one blank in this series, however, presumed to be due to an undiscovered element, in the position just below manganese.

We begin the **third long period** with another inert gas, xenon (Xe), and all goes well for a time, elements of similar properties appearing at regular intervals. Presently, however, **when we reach lanthanum, La = 139.0, we find that no less than fifteen elements are known, where the table provides spaces for but two.**

This situation has occasioned no end of speculation, and considerable ingenuity has been expended in trying to modify the periodic table in such a way as to provide a place for these extra individuals, commonly known as the *rare earth elements* (§ 588). But the difficulty is that they are all so closely related (metals, valence *three*) that they ought to be placed in a single space under their nearest relative, yttrium (Yt).

Following the rare earth elements, the normal course of affairs is resumed, elements of similar properties occurring at regular intervals. Thus by leaving an occasional blank, presumed to represent an undiscovered element, we are able to complete the third period and begin a fourth one, which breaks off abruptly with the element uranium.

167. The Five Types of Elements.*—The **Periodic Table,** just constructed, shows that the 87 known elements belong to 5 main types.

1. At the extreme left of the table are the **inert gases**—elements that fail to unite with any other elements whatever.

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* This topic is developed more fully in § 414.

2. Next to the right of these lie the **light metals**—elements in which metallic characteristics are most pronounced. All of these form *active bases*, which unite with acids to form salts, *not easily hydrolyzed by water* (§ 113). These light metals all migrate toward the *cathode** when a solution of one of their salts is electrolyzed.

The extraordinary contrast between the inert gases and the light metals is symbolized in the table by a blank space between these two groups of elements.

3. In column IIIA are the **rare earths** (§ 588), metallic elements extremely alike, with valence almost uniformly three.

4. In the middle portion of the table are the **heavy metals.** Metallic properties are here less pronounced than with the light metals. Though they unite with oxygen or hydroxyl to form bases, these are relatively inactive. Their salts are thus much more readily hydrolyzed by water than those of light metals. Though the heavy metals commonly migrate toward the *cathode* * during electrolysis, there are some exceptions to this. The properties of the heavy metals, and their relationships to each other, are treated in detail in § 419. We may here merely note that among the heavy metals the contrast between elements in neighboring columns is much less pronounced. In other words, **definite resemblances are frequently to be found between neighboring elements in the same horizontal row.** In Group VIII, indeed, these horizontal relationships are the important ones. Iron (Fe), for example, is closely related to cobalt (Co) and nickel (Ni), and has some important resemblances to manganese (Mn) and chromium (Cr); but is practically unrelated to the two elements (Ru and Os) that occupy positions immediately beneath it.

Note that aluminum, although of low specific gravity, is chemically a heavy metal.

5. Toward the right-hand margin of the table are the **non-metals.** Their properties are the reverse of those of the metals. Their oxides unite with water to form acids; they do not form stable sulfates, nitrates, acetates, etc.; their chlorides are completely hydrolyzed by water. During electrolysis they migrate toward the *anode*.*

168. Group Valences.—We can apply the periodic table in a rough way in determining the valences of the individual elements:

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* Anode, cathode, defined in § 126.

1. **Group numerals *of three or less*** (or the formulas, R_2O, RO, R_2O_3) **represent the *usual valence* of the elements of the given group, and very often their only valence.** Thus, the valence of scandium (Group IIIA) is +3; that of cadmium (Group IIB) is +2. But gold and copper (Group IB) have each an extra valence (Au''', Cu'') in addition to the one indicated by this rule.

2. **Group numerals of *four or more* represent the maximum valence of the elements toward oxygen in stable compounds.** Thus the maximum valence of manganese (Group VII B) is 7 ($KMnO_4$). This maximum valence is commonly manifested only when the element forms an acidic oxide or makes up part of a non-metallic radical. **A valence of two less than the maximum is common among non-metals;** and in many cases a valence of **eight less than the maximum** (thus for S, valences of +6, +4, −2).

3. **The valence of the elements of the *eighth or* transition group is variable, ranging from two to eight.**

Since the three rules just given are subject to several exceptions, and since the heavy metals, in particular, usually manifest other valences, below the one that the rule indicates as a maximum, it may be helpful in individual cases to refer to the small chart at the bottom of the table. This indicates, for instance, that chromium, the twenty-fourth element, has valences of +2, +3, and +6; while germanium, the thirty-second element, has valences of −4, +2, and +4.

169. Another Form of the Periodic Table.—On the opposite page, the preceding arrangement of the elements has been modified in such a way as to bring correspondingly numbered A and B groups together. **To get this result, cut the former table through by a vertical line placed just to the right of Group VIII; then move *the right-hand portion downward half a space, and shove it over*** to the left. The elements formerly in the right-hand portion of the table are thus interpolated between the lines in which the other elements appear. Elements thus transferred are here *italicized.*

170. Practical Applications of the Periodic Table.—1. The periodic table and the generalizations to be drawn from it are of great assistance in the study of chemistry; for **instead of considering the properties of nearly ninety different elements, the student can concentrate his attention on a few that serve as types for the rest.** Thus, the facts we have already learned concerning chlorine (Chap. XII) will help us to remember similar facts concerning the related elements fluorine, bromine and iodine (Column VIIA).

THE PERIODIC TABLE
(Mendelejeff's form, slightly modified)

Group 0	Group I R_2O		Group II RO		Group III R_2O_3		Group IV RO_2	RH_4	Group V R_2O_5	RH_3	Group VI RO_3	RH_2	Group VII R_2O_7	RH	Group VIII RO_4		
	A	B	A	B	A	B	B	A	B	A	B	A	B	A			
He 4	Li 6.94		Be 9.1		B 10.9		*C* 12.005		*N* 14.008			*O* 16.000		*F* 19.0			
Ne 20.2	Na 23.00	●	Mg 24.32		Al. 27.1		*Si* 23.3		*P* 31.04			*S* 32.06		*Cl* 35.46			
A 39.90	K 39.10	*Cu* 63.57	Ca 40.07	*Zn* 65.37	Sc 44.1	*Ga* 70.1	Ti 48.1	*Ge* 72.5	V 50.0	*As* 74.96	Cr 52.0	*Se* 79.2	Mn 54.93	*Br* 79.92	Fe 55.84	Co 58.97	Ni 58.68
Kr 82.92	Rb 85.45	*Ag* 107.88	Sr 87.63	*Cd* 112.40	Yt 89.33	*In* 114.8	Zr 90.6	*Sn* 118.7	Cb 93.1	*Sb* 120.2	Mo 96.0	*Tc* 127.5	?	*I* 126.92	Ru 101.7	Rh 102.9	Pd 106.7
X 130.2	Cs 132.81	*Au* 197.2	Ba 137.37	*Hg* 200.6	La 139.0	*** *Tl* 204.0	Ce 140.25	*Pb* 207.20	Ta 181.5	*Bi* 208.0	W 184.0	?	?	?	Os 190.9	Ir 193.1	Pt 195.2
Rn 222.4	?		Ra 226.0		Ac 230		Th 232.4		Pa 234		U 238.2						

The positions of elements as yet undiscovered are indicated by question marks.

Asterisks indicate the position of omitted rare earth elements.

The most pronounced non-metallic elements lie within the heavy line toward the upper right-hand corner of the table.

This table is due to Mendelejeff, the Russian chemist who first directed attention to many of the relationships we have traced between the elements. For this historical reason it is the one most commonly presented in text-books of chemistry, and the student should take pains to become familiar with it; but it has the disadvantage that it tends to overemphasize the less important relationships, such as the agreement in valence between the otherwise very dissimilar elements potassium and silver. Moreover, the real and important contrasts existing between the heavy metals and the other elements (§ 167) are here obscured. The first form of the table (repeated on the back cover) is therefore the one to which reference will be made in what follows.

2. Historically, the most interesting application of the periodic table has been **in predicting the properties of elements in advance of their discovery.**

Thus, when Mendelejeff published his classification, in 1871, the element germanium was unknown. To make the following elements fall into their proper groups it was necessary to leave a blank in the periodic table where germanium now appears. But the great Russian chemist did more than this. he came out boldly with a forecast of the properties of the undiscovered element—properties which are evidently intermediate between those of silicon and tin. Fifteen years later, a German chemist, Winkler, discovered germanium, and verified the predictions of Mendelejeff to the last particular.

3. Review § 159. Historically, too, the periodic table has been of use **in giving definite information concerning the true atomic weights of the elements**; which, it will be recalled, cannot be determined directly, but are calculated whole multiples of experimentally determined combining weights (§ 162).

Thus the combining weight of glucinum is 4.55, and chemists were for a time in doubt whether the atomic weight should be taken as two or three times that figure. But three times 4.55 is 13.65, an atomic weight which would place glucinum between carbon and nitrogen, where the periodic table provides no place for it. The conclusion is therefore that the atomic weight is 2 × 4.55 = 9.10. This places glucinum definitely in the second group, in the space between lithium and boron.

4. **The technical man, in fields related to chemistry, is apt to make frequent use of suggestions derived from the table.**

Thus, electric stoves, toasters, flat-irons, and other household devices, small electric furnaces, and electrically heated ovens for bakeries, were made possible by the discovery of some new alloys capable of being drawn into wire, hard to oxidize, and of very high melting point. Some of these contain nickel and chromium (§ 525); but the relationship of nickel to cobalt and iron, of chromium to vanadium (horizontal) and to molybdenum (vertical) would suggest cobalt and chromium, iron and chromium, nickel and vanadium, nickel and molybdenum, and other combinations. Most of these alloys have actually been tried, found promising for the purpose named, and patented.

It is apparent that since a patent's power to protect, and therefore its money value, depends very largely on its being drawn in such a way as to anticipate and include all modifications of the original idea likely to be successful, no inventor or patent attorney can afford to neglect suggestions likely to be contained in the periodic table.

171. Atomic Numbers.—The number of the position that an element occupies in the periodic table is called its *atomic number* —one for hydrogen; two for helium, etc. In nearly every case, the order of atomic numbers is the same as the order of increasing atomic weights. But in the case of argon (at. wt. 40) and potassium (at. wt. 39.10) the order of atomic weights has to be reversed in order to bring these elements into the same column with related elements. Two other instances of reversed order of atomic weights (Co and Ni; Te and I) occur in other parts of the table.

The atomic number of an element, and thus its position in the periodic table, may be determined independently of its chemical properties by studying the waves (X-rays) that the element emits when heated to incandescence by a stream of electrons (Fig. 53) in an evacuated tube.

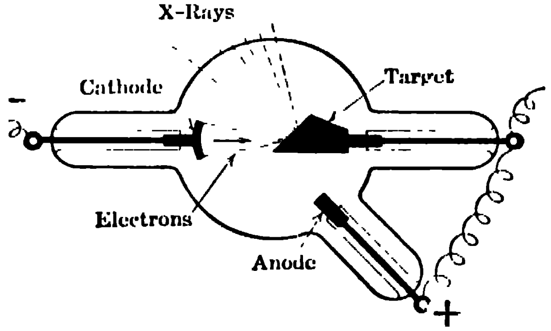

FIG. 41.—An X-ray tube. Practically all the air within the tube has been removed with the aid of a high-vacuum pump, such as that described in § 95. The evacuated space is then found to pass an electric current fairly readily, especially if the cathode is heated (with an electric coil). When a current passes through the tube most of the electricity is conveyed as a stream of electrons, which are shot out from the surface of the cathode with velocities approaching that of light. If this stream is permitted to fall upon a heavy metallic target the latter is raised to incandescence, giving off heat, light, and X-rays. The latter pass through the glass walls of the tube, and may affect a photographic plate outside.

X-rays are now considered to be a disturbance in the ether, caused by the bombardment of the target by the stream of electrons; somewhat as hailstones, when they strike against a window pane, set up an audible disturbance in the atmosphere. X-rays differ from ordinary light in being about a thousand times as rapid in their rate of vibration. What concerns us here, however, is that this rate varies with the material of the target at which the X-rays originate. Moseley, the pioneer in this work (1912), mounted samples of different elements on a small car, which was placed within the tube and moved by a magnet, in such a way as to subject each sample in turn to bombardment by the electrons. The X-rays were reflected from the surface of a crystal (§ 30) and studied with a photographic plate. It turned out that each increase of one unit in atomic number—each advance, that is, of one space in the periodic table—produced a definite constant increase in the *square-root of the vibration rate* of the X-rays. From the X-rays emitted by an element it is thus possible to tell where it belongs in the periodic table.

Thus, it has been made certain that the different elements in the periodic table have really been assigned to correct positions, even in those cases in which these positions lead to a reversal of the order of increasing atomic weight. Incidentally, it seems reasonably sure that there remain only five undiscovered elements, within the limits of our present table. These are there represented by question marks. Whether there may not be undiscovered elements of atomic weight lower than that of hydrogen or higher than that of uranium, it is impossible to say; though there is no reason to believe that such is the case.

172. Isotopes.—Dalton believed that all the atoms of any given element have exactly the same weight (§ 37). On the basis of this postulate, it has been possible to work out the relative weights of the atoms of different elements—the system of atomic weights (§ 162) at present in use. Nevertheless, different atoms of a given element, though of indistinguishable chemical properties, are often of different weights. The atomic weight of the element merely represents the *average weight*, relative to O=16, of the several different types of atoms. It is a constant quantity merely because these different types of atoms, as we meet them in nature, are always intermingled in a constant proportion, and because they are of so nearly identical properties that no chemical reactions enable us to separate them.

Elementary forms of matter which appear to be identical in chemical properties, but which differ in atomic weight and in properties depending on atomic weight, are called **isotopes.**

When positively charged particles are made to move in a vacuum under the influence of electrical and magnetic forces, particles of different masses move in different paths, and produce images in different places on a photographic plate. By this means (*positive-ray analysis*), it has been demonstrated that neon, chlorine, magnesium, and a number of other elements are each a mixture of two or more isotopes. Ordinary lead is now known to be a mixture of isotopes, which are known individually in the different kinds of *radioactive lead*, produced by the disintegration (§ 601) of atoms of radium, actinium, and thorium. The atomic weight of lead thus varies with its origin. Nearly all the elements that have been shown to consist of mixtures of isotopes are those the atomic weights of which are very noticeably different from whole numbers. Hydrogen, nitrogen, oxygen, sulfur, and phosphorus—elements in which the atomic weights are very close to whole numbers—appear to be pure elements. The atoms of any one of these are all of the same weight.

But if the atomic weights of the pure elements are really multiples of one, **it seems very possible that the atoms of all the other elements are made up of atoms of hydrogen; or, more probably,**

of atoms of hydrogen and helium. But definite proof of this has not been given.

All of the isotopes of any given element, such as chlorine, are, so far as our present knowledge goes, identical in their chemical properties, occupy the same position in the periodic table, and have the same atomic number.

The preceding remarks and those of § 11 determine our present definition of an element. **An element is a type of matter not decomposable by any of the means commonly resorted to in decomposing compounds, and having properties that give it a definite, integral atomic number** (§ 171)—which usually means a definite position in the periodic table.

The atoms of a given element may differ in weight, but are believed to be identical in all their chemical properties.

173. The Periodic Law.—If we examine the elements in the order of their atomic numbers, we find the valence rising irregularly to a maximum of seven or eight, then falling off to zero or one, and repeating. This is well presented in the small chart at the bottom of the periodic table. This variation reminds one of the rise and fall of the tides, or the periodic recurrence of summer and winter. In mathematics a quantity that *first increases and then decreases* in a regular way as a second quantity *continues to increase* is called a *periodic function* of the latter, hence the name **Periodic Table.**

These rough analogies led Mendelejeff to state that "the properties of the elements are periodic functions of their atomic weight." This remark is not only meaningless to persons of slight mathematical experience, but overstates the truth. For the atomic weights of the elements are a set of disconnected numbers, that do not form the successive values of a continuous variable. Moreover a function in mathematics is not considered as a periodic one unless the periods are of equal length.

Atomic numbers are a more fundamental property than atomic weights; for all the isotopes of a given element differ in atomic mass, while having the same atomic number. Accordingly, it would seem best to abandon the preliminary form of the Periodic Law, based on atomic weights, as stated at the close of § 165.

The best statement would seem to be: **If the elements are**

arranged in the order of their atomic numbers, elements of similar properties occur at regular intervals.

174. Structure of Atoms.—(This section may be postponed to precede § 260). We have previously (§ 13) directed attention to the presumption that though atoms resist all ordinary attempts to decompose them, they are not to be regarded as indivisible. The present view (§ 125) is that atoms are constructed of unit positive charges of electricity (**protons**) associated with unit negative charges (**electrons**).

Experiments that cannot be described here * make it seem probable that most of the mass of an atom is concentrated in a **nucleus.**

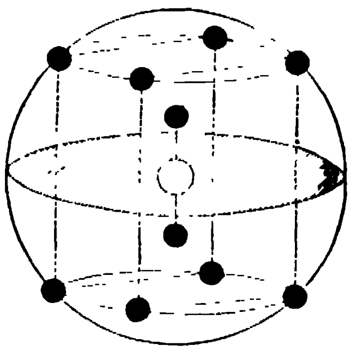

FIG. 15.—An atom of neon, according to the Lewis-Langmuir theory. This is the 10th element in the periodic table. An atom of neon is accordingly believed to consist of a central positive nucleus, containing ten more protons than electrons. Grouped about this, to make the whole atom electrically neutral are ten external electrons, an inner pair, surrounded by a group of eight, occupying the corners of a cube.

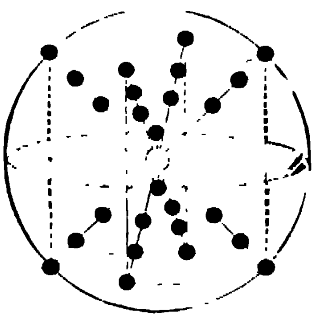

FIG. 16.—An atom of iron. The three concentric groups of eight electrons each are presumed to have something to do with the magnetic properties of iron.

This contains more protons than electrons, to a number corresponding to the atomic number of that element. Thus an atom of iron (atomic number 26) is presumed to possess a nucleus containing 26 more protons than electrons.

Grouped about this nucleus, or perhaps circulating about it in definite orbits, are **external electrons,** equal in number to the atomic number, and therefore to the excess protons in the nucleus. Thus the atom as a whole is electrically neutral.

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* See bibliography of books on the structure of matter, in appendix.

It is presumed (1) **that the nucleus determines the relative mass of an atom (atomic weight).**

(2) **That the number and arrangement of external electrons determine its chemical properties.**

(3) **The different isotopes of an element are presumed to differ in atomic weight because their nuclei are constructed differently; but they are identical in chemical properties because they have identical systems of external electrons.**

Much remains to be learned concerning the manner in which the electrons are disposed within the **sheathe,** or external part of the atom. The evidence of the spectroscope (§ 445) indicates that the electrons of any one atom circulate in a limited number of orbits, and that each spectral line (of the ordinary, as opposed to the X-ray spectrum) represents energy emitted when an electron passes over ("falls in") from one orbit to an inner orbit. This, the **Bohr Theory,** has recently been brought into exact accord with precise measurements of the wave-lengths represented by spectral lines of the elements of simple structure.

In all probability, then, the Bohr Theory contains essentials that will be included in the theories of the future. Yet chemists have been very much interested during recent years in the **Lewis-Langmuir Theory,** which ignores spectral data and represents the electrons as being stationary, or at least as being representable by stationary points, for the purposes for which the theory was conceived. According to this, the most inactive elements, the gases of Group 0, owe their inactivity to an unusually stable arrangement of their external electrons -a stable pair, or a stable pair surrounded by one or two groups of eight (**octets**) occupying the corners of a cube. For the elements of higher atomic numbers, in Group 0, the outermost stable group may contain 8 or 32 electrons. Tabulated, these assumptions appear:

Element of Group 0	*At. No.*	*Groups of electrons, from center outward*
He	2	2
Ne	10	2, 8
A	18	2, 8, 8
Kr	36	2, 8, 8, 18
Xe	54	2, 8, 8, 18, 18
Rn	86	2, 8, 8, 18, 18, 32

By adding one electron to any of the stable groupings just listed, we get the electronic grouping of an element of Group I A. By adding two electrons we get that of an element of Group II A, etc.

To summarize: **According to the Lewis-Langmuir Theory each element has as many stable groups of electrons as the inert gas at the left of the same row, in the Periodic Table of § 166; and, in addition, an outer shell containing as many more electrons as the given element is removed spaces to the right of Group O.**

Ions are formed by atoms or groups of atoms losing or gaining electrons beyond the number that is proper to those elements in the uncharged and uncombined condition; and the **direct union of atoms (non-polar valence,** § 125) is represented as due to electrons shared between neighboring atoms, as shown in Fig. 47.

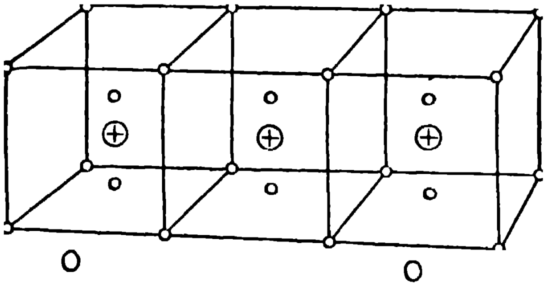


FIG. 47.—A molecule of carbon dioxide An atom of carbon and two atoms of oxygen have come together to share certain electrons in common Thus they have been able to form three stable pairs, surrounded by three stable octets, although the total number of external electrons available is only 22.

EXERCISES

1. State at least three particulars in which two undiscovered elements, one of atomic weight 219, the other of atomic weight 225, will be found to differ sharply.

2. Explain the nature of the difficulty met in placing the rare earth elements in the periodic system.

3. Give a statement of the principal valence relations of the periodic table, stating whether the indicated valence is the usual one, or a maximum.

4. Indicate the valence (+ or −) of each element in the following formulas, and show that this valence was to be expected from the position of the element in the periodic table:

SnO_2, AsH_3, TiO_2, PbO_2, H_2PtCl_6, $K_2Cr_2O_7$, NH_3, HNO_3,
HBO_2, $AuCl$, K_2FeO_4, I_2O_5, NH_4VO_3, $Bi(OH)_3$, $La(NO_3)_3$.

5. What synonyms are in common use for the words metal and non-metal, respectively?

6. Are the rare earth elements to be regarded as isotopes of a single element? Why or why not?

7. Describe the work of Moseley in the determination of atomic numbers.

8. Tell something of the supposed atomic structure of aluminum.

9. Name in order the nine elements of lowest atomic weight, and describe the characteristics of each. Which of these elements form oxides? Which chlorides, stable in the presence of water? Which dissolve in sulfuric acid to form sulfates?

10. From analogies suggested by the periodic table, write formulas for such of the following compounds as you believe to exist. If you believe any of them to be non-existent, tell why:

Silicon hydride, germanic oxide, selenic acid, phosphorus nitrate, rubidium sulfate, beryllium acetate, vanadium pentoxide, argon fluoride

11. Explain how the periodic table may serve as a check on the atomic weight of an element? What other check do we have on atomic weights?

CHAPTER XIV

CHLORINE—A TYPICAL NON-METAL

175. Discovery of Chlorine.—In 1774 the Swedish chemist Scheele—one of the discoverers of oxygen (§ 47)—found that by heating hydrochloric acid, sometimes called **muriatic acid,** with any one of a number of oxidizing agents (such as MnO_2) one may obtain *a greenish-yellow gas, with a powerful, irritating odor.* Since this new substance was prepared by the use of an oxidizing agent, what more natural than to suppose that it contained oxygen, whence the name, *oxymuriatic acid gas.*

For more than forty years, chemists accepted this explanation of what happens when hydrochloric acid is oxidized. Then Sir Humphry Davy, the leading English chemist of a century ago, brought conclusive proof that the greenish-yellow gas was an element, to which he gave the name **chlorine** (Greek, *yellow-green*).

The story of how Davy upset the older view concerning chlorine is an interesting example of how a chemist reasons when he sets out to discover something new. If oxymuriatic acid gas really contained oxygen, then it should have been able to pass this on to other elements, forming *oxides.* But though metals could be made to burn in the gas, the product was never a metallic oxide; and when purified charcoal was raised to a white heat, and the gas passed over it, there was practically no action, and no more than traces of the oxides of carbon were formed.

Again, when the gas was heated with hydrogen, one would have expected water to be formed, were oxygen present. But the product obtained was hydrogen chloride, and this alone.

Thus it was concluded that the greenish-yellow gas under investigation was quite free from oxygen, and presumably an element, which could unite directly with hydrogen. Its formation from hydrogen chloride by the use of oxidizing agents was then to be explained by assuming that these gave up oxygen, which *displaced* the chlorine from combination with the hydrogen:

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$

176. How Chlorine Occurs in Nature.—Chlorine never occurs *free* in nature, i.e., uncombined with other elements. It is far too active for that. But combined with metallic elements to form chlorides it exists in inexhaustible quantities.

1. The ocean, covering three-fourths of the earth's surface to an average depth of three miles, contains 2.8 per cent of common salt and 0.8 per cent of other metallic chlorides. This amounts to about *six million cubic miles of solid salt,* containing about 18,000,000,000,000 tons of chlorine. Even a very small arm of the sea contains a vast amount of dissolved solids. Long Island Sound, with about 50 cu. mi. of water, could furnish three million tons of sodium chloride.

2. Innumerable salt lakes, salt wells, and beds of solid salt are known and worked in every part of the world. Such salt deposits were formed during past geological ages by the evaporation of water contained in arms of the sea that were cut off and surrounded by land. In this country, salt is generally mined by sinking shafts to the deposits and pumping in water to form a saturated solution. This solution is brought to the surface, purified, and evaporated in vacuum pans, or used in the preparation of caustic soda and chlorine by the electrolytic process presently to be described.

3. We find chlorine combined as *hydrogen chloride* in the gases belched forth by volcanoes. Certain streams on the slopes of the Andes carry away many tons of dissolved hydrogen chloride each day, and are so acid that no fish can live in them.

4. Hydrochloric acid is secreted by the stomach and its glands as a constituent of the gastric juice— enough in a single day to make a fatal dose, if taken in concentrated form, by way of the mouth.

HYDROGEN CHLORIDE

177. Preparation of Hydrogen Chloride.—Before taking up chlorine itself we shall describe the preparation and properties of hydrogen chloride. This is prepared:

1. **In the laboratory.** (*a*) By the action of sulfuric acid on common salt, using the apparatus described in § 105.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow .$$

(*b*) By dropping concentrated hydrochloric acid on granular calcium chloride, contained in a flask. The calcium chloride abstracts water from the hydrochloric acid, and hydrogen chloride gas escapes in a steady stream.

(*c*) By treating fused ammonium chloride in a Kipp apparatus (§ 71) with concentrated sulfuric acid.

Write equation.

2. **Commercially,** by the action of sulfuric acid on common salt, in two stages.

The salt is mixed with the sulfuric acid and gently heated within an iron pan (*A*) set in brickwork, as shown in Fig. 48. The reaction that takes place here is that formulated above for the laboratory method.

When the reaction ceases, the solid residue of *sodium acid sulfate*, with an excess of unchanged *sodium chloride*, is transferred to *muffle furnaces* (*B*, *B*) and heated to a higher temperature. Here a further reaction takes place, yielding *normal sodium sulfate*, commonly called salt-cake, a material used in the manufacture of glass (§ 402):

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl \uparrow .$$

This final stage cannot be realized on a small scale in the laboratory, since it requires a temperature at which glass begins to soften. The gas liberated in these two reactions is carried away by a current of air, and absorbed in water, yielding a rather impure (*commercial*) hydrochloric acid.

178. Physical Properties of Hydrogen Chloride Gas.—1. Hydrogen chloride is a **colorless** gas, **about one-fourth heavier than air.**

Check this statement, by calculation (§ 154). Show that hydrogen chloride is only a little more than half as dense as chlorine.

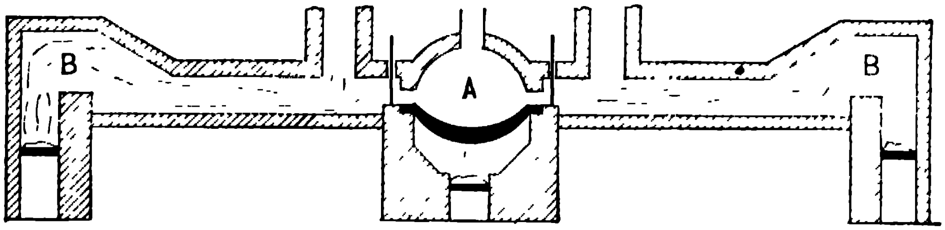


FIG. 48.—Commercial preparation of hydrochloric acid.

2. **It can be condensed to a liquid by pressure alone,** being much more easily liquefied than nitrogen, oxygen, or hydrogen, but not quite so easily as chlorine or ammonia.

3. Inhaled in traces, it has a **suffocating odor.** The inhalation of any considerable amount will cause intense pain.

4. It **fumes in moist air.** Other related gases (HF, HBr, HI) behave in the same way, the fumes being really clouds of minute droplets of liquid hydrochloric acid, formed by solution of the gas in the water vapor of the atmosphere.

5. Hydrogen chloride is **extremely soluble in water.**

A lecture experiment to demonstrate this is shown in Fig. 49. A round-bottomed flask is filled with the gas, closed with a rubber stopper carrying a long glass tube, and inverted over a large beaker of blue litmus solution. If a few drops of water are introduced into the flask by means of a medicine dropper (*A*), a part of the gas immediately dissolves, creating a partial vacuum. Atmospheric pressure then forces a fountain of litmus solution from the beaker up into the flask. That the solution of hydrogen chloride thus formed is an acid (hydrochloric acid) is shown by the fact that the liquid forming the fountain turns from blue to red.

179. Hydrochloric Acid.— Hydrochloric acid is given the formula HCl, the same as hydrogen chloride gas; for the latter is assumed merely to dissolve in an indefinite amount of water, without entering into chemical combination with it. It is recognized by the fact that it unites with ammonia (NH_3) to form a white **cloud** (ammonium chloride, NH_4Cl); though the related substances, HBr, HI—in fact *any easily volatile acid*—will do the same thing.

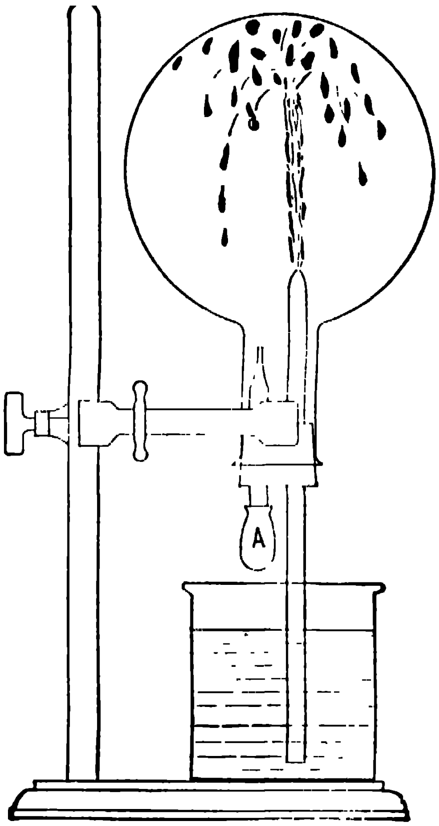


FIG. 49.

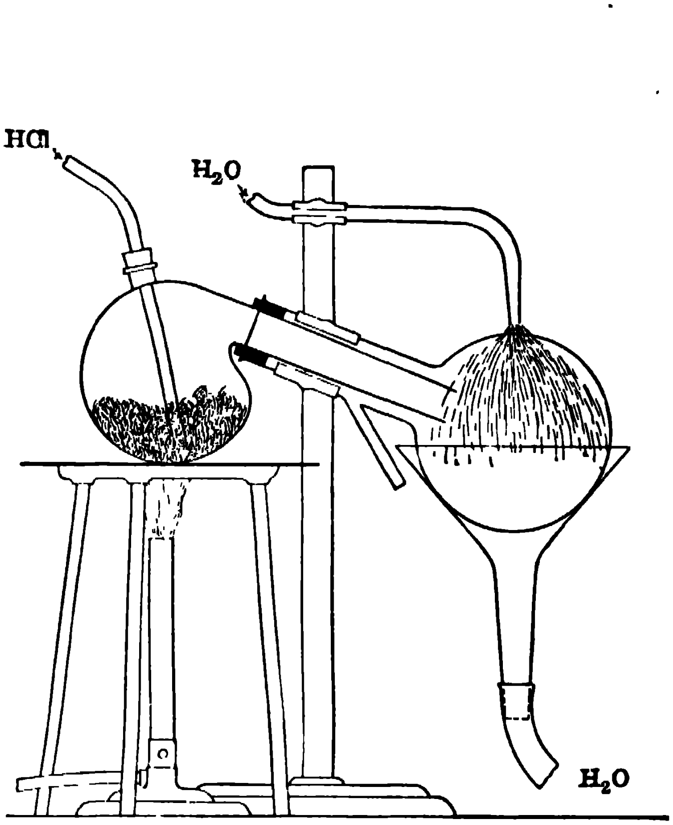


FIG. 50.

FIG. 49.—Lecture experiment to illustrate the extreme solubility of hydrogen chloride in water.

FIG. 50.—Preparation of anhydrous aluminum chloride. Aluminum turnings, contained in a retort, are heated in a current of hydrogen chloride. The neck of the retort must be rather wide, or it will be stopped up by the aluminum chloride produced.

The principal chemical properties of hydrochloric acid, ***shared by other active acids***, may be illustrated as follows:

1. **It reacts with metals above hydrogen in the electrochemical series of § 72,** liberating hydrogen:*

$$Zn + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2$$

Even hydrogen chloride gas, in absence of more than traces of water, is similarly decomposed by metals (Fig. 50).

$$2Al + 6HCl = 2AlCl_3 + 3H_2 \uparrow .$$

2. **It reacts with carbonates and sulfites, liberating carbon dioxide and sulfur dioxide gases:**

$$\underset{\text{Calcium carbonate}}{CaCO_3} + 2HCl = \underset{\text{Calcium chloride}}{CaCl_2} + H_2O + CO_2 \uparrow .$$

$$\underset{\text{Calcium sulfite}}{CaSO_3} + 2HCl = CaCl_2 + H_2O + SO_2$$

3. **It reacts with metallic oxides and metallic hydroxides to form *chlorides* and *water*.**

$$MgO + 2HCl = \underset{\text{Magnesium chloride}}{MgCl_2} + H_2O.$$

$$KOH + HCl = KCl + H_2O.$$

The chlorides of sodium, potassium, calcium, etc., are neutral toward litmus. Solutions of the chlorides of the heavy metals (iron, copper, lead, etc., are acid toward litmus). Explanation, § 114.

CHLORINE

180. Preparation of Chlorine by Oxidation of Hydrochloric Acid.—Chlorine is still prepared in the laboratory by the method by which it was first produced by Scheele, a century and a half ago: **action of oxidizing agents on hydrochloric acid.**

1. The oxidizing agent most commonly used for this purpose is **manganese dioxide,** MnO_2. This is mixed with common salt and treated with sulfuric acid in a flask fitted with a thistle-tube,

T, and delivery tube (Fig. 51). The sulfuric acid, added through the thistle-tube, first acts upon the salt, liberating hydrogen chloride, which immediately reacts with the manganese dioxide:

$$H_2SO_4+NaCl = NaHSO_4+HCl.$$

$$4HCl+MnO_2 = 2H_2O+Cl_2 \uparrow +MnCl_2.^*$$

The chlorine is collected, like hydrogen chloride (§ 105), by displacement of air. A tube, *B*, filled with alternate layers of charcoal and slaked lime, serves to absorb any chlorine that would otherwise escape into the room.

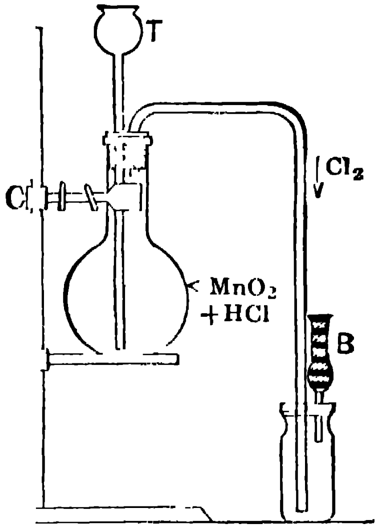


Fig. 51.—Laboratory preparation of chlorine.

2. Other common oxidizing agents are **potassium permanganate,** $KMnO_4$, and **potassium dichromate,** $K_2Cr_2O_7$. These are placed in a flask, concentrated hydrochloric acid is added through a dropping funnel, and the mixture is heated:

$$16HCl+2KMnO_4 = 8H_2O+5Cl_2+2KCl+2MnCl_2.$$

$$14HCl+K_2Cr_2O_7 = 7H_2O+3Cl_2+2KCl+2CrCl_3.$$

Such methods are too expensive to be of commercial value. They do have the practical advantage, however, of being easily controlled, for the evolution of chlorine begins only when the flask is warmed, and stops almost as soon as the heating is discontinued.

---

* With an excess of sulfuric acid, the $MnCl_2$ is finally converted into $MnSO_4$.

3. It is interesting to notice that chlorine may be displaced from hydrogen chloride even by the **oxygen of the air, in the presence of certain catalytic agents.**

Thus, if a mixture of air and hydrogen chloride, formed by bubbling air through concentrated hydrochloric acid, is passed through a heated glass tube containing asbestos fiber soaked in cupric chloride solution (catalyzer) the gas issuing from the other end of the tube will have a slight greenish color, and will answer to other tests by which we recognize chlorine:

$$4HCl+O_2 \rightleftarrows 2Cl_2+2H_2O.$$

This reaction was formerly used for the preparation of chlorine on a large scale (*Deacon process*) but had the disadvantage of being reversible, and therefore incomplete. Moreover, chlorine is now prepared so cheaply by electrolysis that it would not pay, at least in the United States, to make it from hydrochloric acid. The problem is rather to cause waste hydrogen and chlorine to combine to form hydrogen chloride.

4. Nitric acid also reacts with hydrochloric acid to liberate chlorine (§ 301).

Notice that these different methods for the preparation of chlorine from hydrogen chloride may all be summarized under one general rule: **Whenever hydrochloric acid is treated with an oxidizing agent, the products are *chlorine*, *water*, and the *chlorides* of any metals contained in the oxidizing agent.** Observe, furthermore, that **the direct oxidation of hydrochloric acid never gives such products as $HClO$ or $HClO_3$.**

181. The Preparation of Chlorine by Electrolysis.—Review § 65. When an electric current is passed through a solution of sodium chloride in water, chlorine is evolved at the anode and hydrogen at the cathode, leaving sodium hydroxide (caustic soda) behind in the solution:

$$2NaCl+2H_2O \rightarrow 2NaOH+\underset{\text{Cathode}}{H_2}\quad\underset{\text{Anode}}{Cl_2}.\uparrow$$

A discussion of why we get these three products rather than sodium and chlorine will be given later (§ 127).

In the Nelson cell, the electrolyte is contained in a narrow steel tank containing a number of graphite anodes immersed in brine, and separated from the perforated sheet-iron cathode by a diaphragm of closely-woven asbestos cloth. The hydrogen and sodium hydroxide, formed at the surface of the cathode, are effectively separated by the asbestos cloth from the chlorine liberated at the anode, thus preventing a reaction (§ 181) that would form an undesirable product, sodium hypochlorite.

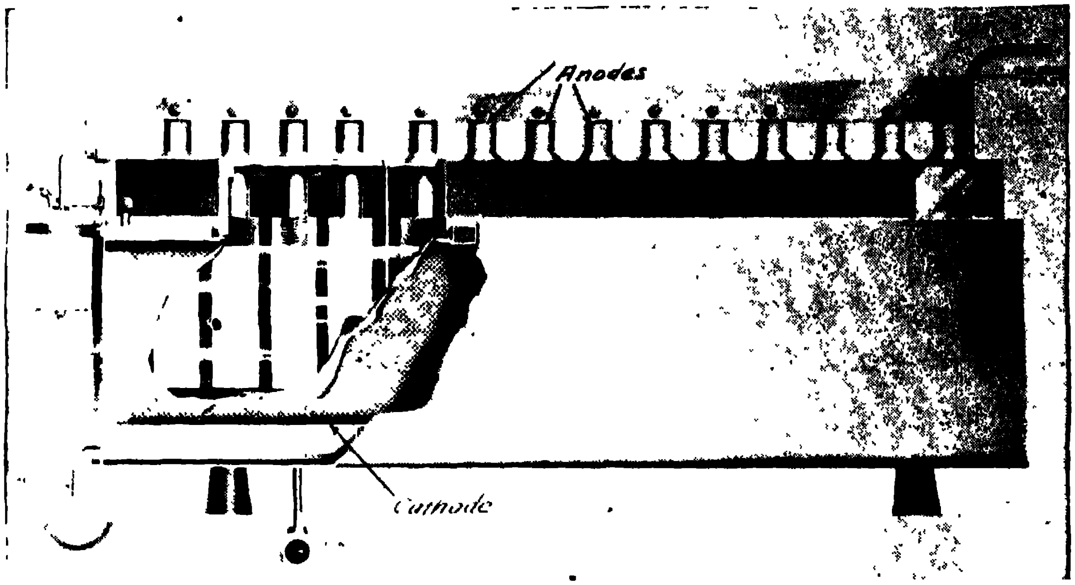


FIG. 52.—The Nelson cell, for the production of chlorine and caustic soda by electrolysis of a solution of common salt.

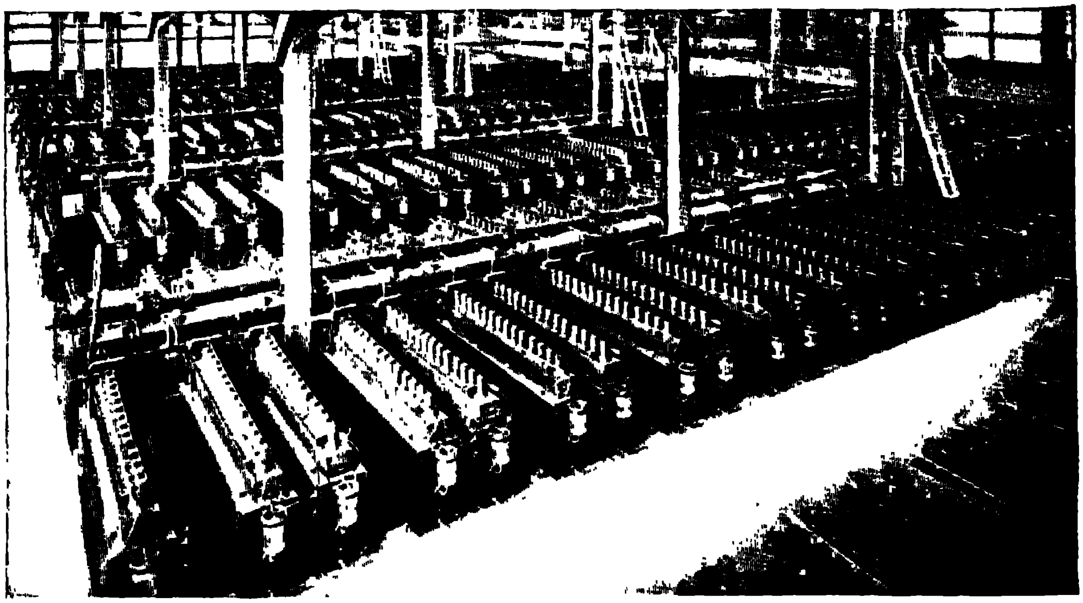


FIG. 53.—One of the eight cell rooms at Edgewood arsenal. The entire plant was planned to contain over 3000 cells, capable of producing 100 tons of liquid chlorine, and a somewhat larger amount of solid caustic soda, each day.

The chlorine from the electrolytic cells passes by way of a tile gas-main through cooling chambers into a tower down which concentrated sulfuric acid trickles, and is thus dried. Dry chlorine is without effect on most metals, at ordinary temperatures, and may be put through compression pumps and transported in cast-iron mains, or in liquid form in lead-lined cylinders or tank-cars.

Of the three products obtained by the electrolysis of brine, sodium hydroxide is always in greatest demand in time of peace. Chlorine and hydrogen are mere by-products, obtainable in quantities more than sufficient to satisfy the market. The greatest electrolytic installation ever known, however, was put into operation during the war at Edgewood Arsenal, in Maryland, with chlorine as its most important objective. The hydrogen in this and most other plants has been permitted to run to waste.

182. Physical Properties of Chlorine.—1. Chlorine is a **greenish-yellow** gas, which **may be condensed to a yellow liquid** by about six atmospheres of pressure at room temperature.

2. It has an irritating odor, and is **very poisonous.**

3. It is about two and one-half times as heavy as air.

4. Cold water dissolves about twice its own volume of chlorine. Hot water dissolves very much less.

If a solution of chlorine in water is cooled in ice, greenish crystals of *chlorine hydrate* separate. These have the composition $Cl_2 \cdot 8H_2O$. This substance was employed by Faraday to produce liquid chlorine. The crystals were placed in one arm of a sealed tube having the shape of an inverted V (Fig. 54) and were there gently heated while the other arm of the tube was cooled in ice. Presently the crystals melted, forming a layer of liquid chlorine below the layer of water (the two substances being but very slightly miscible, § 121). The liquid chlorine then evaporated and condensed in the cold arm of the tube.

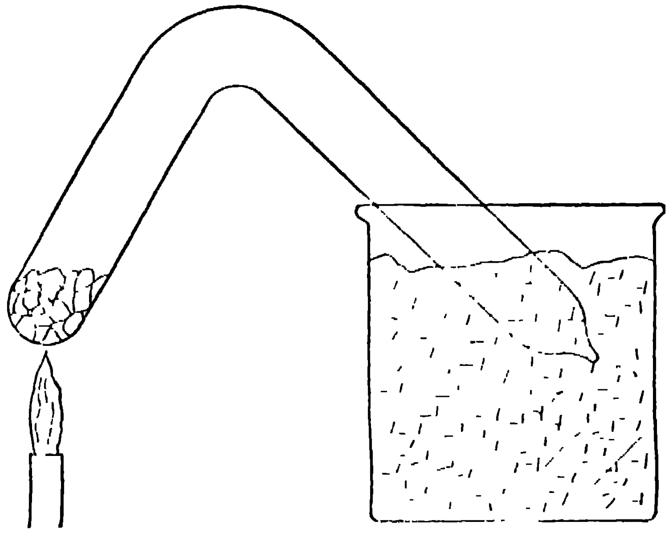


FIG. 54.—The method by which chlorine was first liquefied (Faraday).

183. Direct Union of Chlorine with Other Elements.—1. *With Hydrogen.* When chlorine is mixed with hydrogen no action takes place, so long as the mixture is kept in the dark. In diffused sunlight the two gases combine slowly to form hydrogen chloride:

$$H_2 + Cl_2 = 2HCl.$$

In direct sunlight, or in the light of a burning magnesium ribbon, the reaction is instantaneous—an **explosion.** As a lecture experiment, a small flask containing a mixture of hydrogen and chlorine, previously filled in the dark, may be safely exploded if placed within a closed basket of fine wire gauze, to retain the flying fragments of glass.

2. *With Metals.* When metallic **antimony** is thrown into a jar containing chlorine gas, the metal catches fire at once, forming **poisonous** white fumes, mainly antimony pentachloride, $SbCl_5$. Similarly, metallic **mercury** is attacked at ordinary temperatures, becoming covered with a white scum of mercurous chloride, HgCl. For this reason it is impossible to collect chlorine gas over mercury.

A small flask, containing a little **gold-leaf,** is partly evacuated by means of an air pump. If some chlorine gas is then admitted, no action on the gold-leaf takes place if the chlorine is perfectly dry, but on the admission of a drop of water the leaf suddenly dissolves (forming auric chloride, $AuCl_3$).

This is one of the many reactions in which traces of water are necessary. As a matter of fact, **most metals are not attacked by perfectly dry chlorine.** Sodium may even be melted in an atmosphere of dry chlorine, without any combination taking place.

3. *With Non-metals.* **Phosphorus** burns in chlorine to form phosphorus trichloride, PCl_3, a liquid; and phosphorus pentachloride, PCl_5, a solid. **Sulfur** burns in a limited supply of chlorine to form sulfur monochloride, S_2Cl_2. This liquid has been used as a solvent for sulfur, in vulcanizing rubber (§ 353).

If a piece of *charcoal* (carbon), held on the end of a heavy copper wire, is heated in the air in the flame of a Bunsen burner, the charcoal will catch fire, but the copper is only very slowly oxidized. If we now thrust the material into chlorine we find the reverse to be true. The charcoal stops glowing, for chlorine will not unite with carbon directly (§ 175); but the copper gives off torrents of greenish smoke, uniting with the chlorine to form a solid compound, cupric chloride:

$$Cu + Cl_2 \rightarrow CuCl_2.$$

If a piece of filter paper is moistened with warm *turpentine* ($C_{10}H_{16}$) and dropped into a jar of chlorine, there is a sudden reaction, evolving black smoke. The chlorine has united with the hydrogen of the turpentine, forming hydrogen chloride, and setting the carbon free. This shows again the inertness of carbon toward chlorine.

Note that in all the preceding reactions of chlorine, another element has its valence increased. This is oxidation (§ 133).

Accordingly, **elementary chlorine serves as an oxidizing agent.** In such cases it is itself *reduced*, decreasing in valence from 0 to −1.

184. Action of Chlorine on Water and Bases.—When chlorine is dissolved in water it reacts to some extent with the latter **to form hydrochloric acid, HCl, and hypochlorous acid, HClO.** This is proved by the fact that the solution will neutralize bases. But the solution retains the greenish color of chlorine gas, an indication that the reaction producing the HCl and HClO must be **incomplete:**

FIG. 55.—A plant for liquefying chlorine. Cylinders of liquid chlorine in foreground.

$$Cl_2+H_2O \rightleftarrows HCl+HClO.$$

So long as nothing happens to disturb the equilibrium, the four substances remain in contact with each other indefinitely. But hypochlorous acid is very unstable, decomposing to form hydrochloric acid and oxygen:

$$2HClO = 2HCl+O_2\uparrow.$$

This decomposition is accelerated by sunlight. Accordingly an aqueous solution of chlorine that is subjected to the action of light will presently lose all its green color, and be converted into dilute hydrochloric acid.

If for chlorine and *water* we substitute chlorine and a *base*, such as KOH, then instead of HCl and HClO we get the corresponding salts (and water):

$$Cl_2+2KOH = \underset{\text{Potassium chloride}}{KCl} + \underset{\text{Potassium hypochlorite}}{KClO} + H_2O.$$

But **if the solution is warmed, the hypochlorite is changed into a chlorate.**

The hypochlorites and chlorates are discussed in the next chapter (§§ 205, 206).

185. Bleaching by Chlorine.—One of the most important applications of chlorine is in bleaching cotton and linen goods, preparatory to dyeing. The best grades of paper are frequently bleached during manufacture.

This property of chlorine may be shown by hanging some strips of litmus paper or moist, colored calico in a cylinder of the gas. The color is usually completely discharged in a few minutes. Printer's ink, which consists largely of carbon, is not affected by chlorine; neither are most natural mineral pigments.

It is significant that **dry chlorine does not bleach dry cloth.** This is believed to indicate that **the bleaching is preceded by the formation of hypochlorous acid,** by the action of the chlorine on water. It is the **chlorine of hypochlorous acid,** and not elementary chlorine, which is the real oxidizing agent, decreasing in valence (§ 133) from +1 to −1.

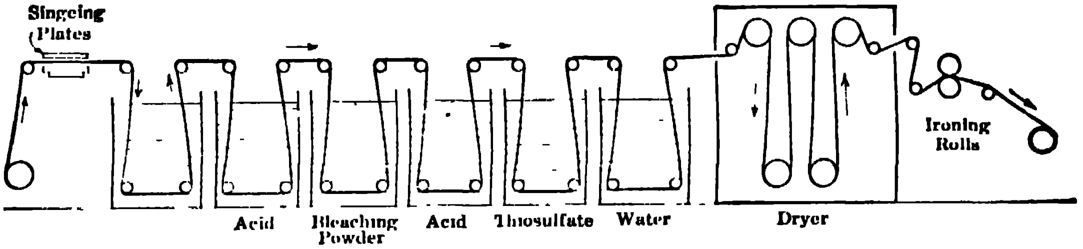


FIG. 56.—How cotton cloth is bleached, in preparation for dyeing.

Cotton cloth, as it comes from the mill, is yellowish and unfit for direct dyeing. It is first singed, to remove the downy pile or fuzz from the surface. It is then passed through a boiling solution of lime-water or sodium carbonate to remove grease and resinous matter, through dilute hydrochloric acid to neutralize the lime, through a solution of bleaching powder, then dilute acid which reacts with the bleaching powder and liberates hypochlorous acid. Extremely thorough washings (not shown in the figure) intervene between these successive stages in the bleaching process. After a final washing, the cloth is treated with a little sodium thiosulfate solution (antichlor) to remove any traces of chlorine that may remain in it.

186. Tests for Chlorides and Chlorine.—1. **Hydrochloric acid, or any metal chloride,** when dissolved in water, will give a white cloud or curdy precipitate (silver chloride) if a few drops of **silver nitrate solution** are added:

$$\begin{array}{ccccccc} \mathrm{KCl} & + & \mathrm{AgNO_3} & = & \mathrm{AgCl}\downarrow & + & \mathrm{KNO_3}. \\ \text{Potassium} & & \text{Silver} & & \text{Silver} & & \text{Potassium} \\ \text{chloride} & & \text{nitrate} & & \text{chloride} & & \text{nitrate} \end{array}$$

To make sure that this precipitate is really silver chloride, it is necessary to make a further test. The liquid is poured through a filter paper to separate the precipitate; then the filtrate is set aside and an empty test-tube placed under the funnel. Now, on adding a little dilute *ammonium hydroxide*, the precipitate should dissolve completely; but the solution thus formed, collecting in the test-tube below the funnel, should give a new precipitate, as soon as the ammonium hydroxide it contains has been neutralized with a slight excess of any acid.

Mercurous nitrate, $HgNO_3$, and *lead nitrate*, $Pb(NO_3)_2$, may also be used as tests for chlorides, for they too give white precipitates with hydrogen chloride or any metallic chloride.

Review § 122. Write and balance equations for the reactions of silver acetate, mercurous nitrate and lead nitrate, respectively, with hydrogen chloride, calcium chloride, and aluminum chloride.

2. **When *chlorine gas* is present in air in considerable concentration, it may be recognized by its color and odor. When present only in minute traces, it is easily detected by bubbling the air through a solution of potassium iodide.** Iodine is then liberated in quantities exactly equivalent to the chlorine in the air, and colors the solution *yellow* or *brown:*

$$2KI+Cl_2=2KCl+I_2.$$

If a little dissolved *starch* is present in the solution, along with the potassium iodide, it will be turned blue by the iodine that is liberated. Sometimes filter paper is dipped into a solution containing potassium iodide and starch, and afterward dried in an atmosphere free from chlorine. If a strip of this *test-paper* is moistened and hung up in a room in which small amounts of chlorine are present, it will presently be turned blue. It must be remembered, however, that the property of liberating iodine from potassium iodide and of thus acting indirectly upon starch is not confined to chlorine. Hydrogen peroxide, ozone, nitric oxide, bromine, and many other substances– in fact *oxidizing agents in general*—will do the same thing.

A solution of chlorine gas in water always gives a faint precipitate with silver nitrate solution. Explain.

Summary:

Tests for **chlorides**: $AgNO_3$ produces $AgCl$, soluble in NH_4OH;
$HgNO_3$ produces $HgCl$, turned black by NH_4OH;
$Pb(NO_3)_2$ produces $PbCl_2$, dissolved by hot water, remaining white in NH_4OH.

Test for **chlorine**: Starch KI paper—turned blue.

How would you distinguish between three solutions, one KI, one KCl, one $AgNO_3$?

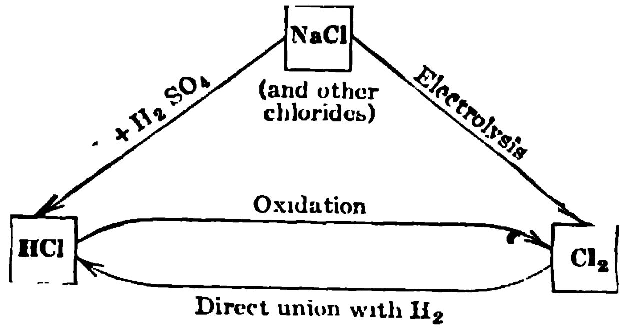
187. Uses of Hydrochloric Acid and Chlorine.— Hydrochloric acid competes with sulfuric acid for the honor of being the world's most important acid. It is used in very large quantities for the purification of bone-black, which is employed in the manufacture of white sugar (§§ 327, 367); for extracting glue from bones; for preparing glucose syrup from corn starch (§§ 368, 369); and for making ammonium chloride, thousands of tons of which are consumed in the manufacture of dry-cells. Metals are frequently prepared for enameling by pickling in hydrochloric acid.

Chlorine is still placed on the market chiefly in the form of bleaching powder; but this is tending to be displaced by liquid chlorine, for bleaching cloth and paper and for sterilizing water. Large quantities are used in the manufacture of sulfur monochloride (§ 183), dyestuffs (§ 372), hypochlorites (§ 205), and chlorates (§ 207). Another important use is in recovering tin from tin scrap (§ 569).

Almost all the toxic "gases" employed in the Great War were volatile liquids, containing chlorine. Chief of these were:

Phosgene, $COCl_2$.
Mustard gas, $Cl \cdot C_2H_4 \cdot S \cdot C_2H_4 \cdot Cl$.
Tear gas (chlorpicrin), CCl_3NO_2.

188. Graphical Summary.



	Hydrogen Chloride	Chlorine
Test	$AgNO_3$	starch, KI
Action on hydrogen	none	direct union
Action on metals	hydrogen replaced	direct union
Action on non-metals	none	direct union
Action on water	dissolves	forms HCl and HClO (action reversible).
Action on bases	forms chlorides	forms chlorides and hypochlorites (cold); or chlorides and chlorates (hot).
Uses	(§ 187)	(§ 187)

EXERCISES

1. Saturated brine contains 26 per cent NaCl by weight. How many tons of water need to be evaporated for every ton of salt produced?

2. A salt well produces brine containing 20 per cent NaCl, 0.4 per cent NaBr, and 1.5 $MgCl_2$ by weight. This brine is concentrated until three-fourths of the NaCl crystallizes out, practically pure. The mother liquors weigh one-fifth as much as the original brine. Calculate their percentage composition.

3. What salt deposits are found in your own state, and how are they mined? Where is the nearest electrolytic soda plant? What disposition is made of the chlorine and hydrogen?

4. What happens, in general, when an oxidizing agent acts on hydrochloric acid? Illustrate with equations, using the following oxidizing agents: sodium chromate, calcium permanganate, red lead oxide (Pb_3O_4), air, lead dioxide (PbO_2).

5. Define oxidation and reduction with respect to valence change. Which element is oxidized and which reduced when zinc dissolves in hydrochloric acid?

6. From the formula of chlorine and its atomic weight calculate the weight of a liter of chlorine at standard conditions. What is the weight of a liter of phosgene, $COCl_2$, at standard conditions? Are the weights thus calculated accurate or only approximate? Why?

7. Calculate the relative heaviness of phosgene with respect to air.

8. Write formulations to represent the reaction to be expected between chlorine and each of the following substances: copper, sulfur, phosphorus, potassium hydroxide, ferrous chloride, potassium iodide.

9. Distinguish between a test for a chloride and a test for chlorine, illustrating each by an equation.

10. Tell how the following substances may be prepared, and write equations: sodium hydrogen sulfate, normal sodium sulfate, chlorine, silver chloride, sodium hypochlorite, ammonium sulfate.

11. Write equations for the preparation of the following substances by methods described in this chapter: mercurous chloride, lead chloride, ammonium chloride, magnesium chloride, zinc chloride, aluminum chloride, potassium chloride. Tell whether the reaction is complete or incomplete in each case, and why.

12. From your study of analogous reactions (§ 179) predict the names of the products that are formed when hydrochloric acid reacts with: potassium sulfite, zinc carbonate, metallic magnesium, ferric hydroxide, barium oxide, ozone (§ 60). Write and balance equation in each case.

13. Explain how sulfuric acid or calcium chloride is able to liberate hydrogen chloride from a concentrated solution of hydrochloric acid.

14. How would you distinguish between four solutions, one containing sodium nitrate, one silver nitrate, one mercurous nitrate, and one lead nitrate (§ 186)?

15. How would you prepare lead chloride from each of the following, in one step, or in several steps: metallic lead, lead carbonate, lead hydroxide, lead nitrate? Write equations.

CHAPTER XV

THE HALOGENS *

Chlorine and oxygen are much alike in uniting directly with metals, nonmetals, and hydrogen in energetic reactions that take place with the evolution of heat and light. But, all things considered, the nearest relatives of chlorine are the elements fluorine, bromine, and iodine (Column VII A of the Periodic Table).

189. Halogens, Halogen Hydrides, and Hydrohalogen Acids. — The four elements fluorine, chlorine, bromine, and iodine are called halogens (Greek, *salt-formers*) because the three last named are found in combination with metals, in the impure salt obtained by evaporating sea-water. Note especially the order in which they are here named which is the order of increasing atomic weights. Sometimes we speak of them as the **halogen family,** because of the striking similarities that exist between them.

The halogens, in the free or elementary condition, are all **colored.** Fluorine is a yellow gas; chlorine a greenish-yellow gas; bromine a dark red liquid; iodine a purplish-black solid. But the compounds formed by the union of the halogens with hydrogen are all **colorless gases.** These are the **hydrogen halides**:

Hydrogen fluoride, HF or H_2F_2
Hydrogen chloride, HCl
Hydrogen bromide, HBr
Hydrogen iodide, HI

These hydrogen halides are all extremely soluble in water (§ 178)—500 or 600 volumes in one volume of water, at ordinary temperatures. The solutions thus formed are the **hydrohalogen acids**—hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydriodic acid. These are very much alike in their properties (§ 192). Their salts (NaF, $MgBr_2$, AlI_3, etc.) are collectively known as **metallic halides.**

Hydrogen fluoride differs from the other hydrogen halides in its tendency for two molecules to associate (§ 157) to form complex molecules of the formula H_2F_2. It is an extremely poisonous substance, causes very painful burns if dropped on the skin, and will etch glass. Nevertheless it is *much less active chemically than the other hydrohalogen acids.* Sodium fluoride, for example, reacts alkaline toward litmus (§ 114).

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* In brief courses, most of this chapter may be omitted, since the previous discussion of chlorine gives an indication of the properties of the halogens *in general.*

190. Preparation of the Hydrohalogen Acids from their Salts.—1. We would expect to be able to prepare all the hydrohalogen acids by the method we used for preparing hydrochloric acid (§ 177)—namely by **heating any metallic halide with a non-volatile acid.** Thus if powdered calcium fluoride is mixed in a lead dish with concentrated sulfuric acid, we obtain a colorless gas which fumes in the air, produces a white cloud with ammonia gas, and dissolves readily in water. These are all properties we should expect **hydrogen fluoride** to possess, from its known resemblance to hydrogen chloride. We accordingly formulate the equation:

$$CaF_2+H_2SO_4=CaSO_4+2HF\uparrow.$$

2. If we attempt to prepare **hydrogen bromide** by heating crystals of some bromide in a test-tube with concentrated sulfuric acid, the result is not so satisfactory. At first we get a colorless gas, fuming in the air, and possessing the other properties to be expected of hydrogen bromide. But red vapors appear. Evidently **bromine** is being produced. Nevertheless if the sulfuric acid is somewhat diluted with water (sp. gr. of solution 1.4) very little of the red fumes of bromine appear. The reaction may accordingly be formulated:

$$NaBr+H_2SO_4=NaHSO_4+HBr\uparrow.$$

3. If we attempt to prepare **hydrogen iodide** by pouring sulfuric acid over crystals of sodium iodide there is some evidence of the formation of **hydrogen iodide.** But the purplish vapors of **iodine** appear in considerable quantities, even if the sulfuric acid has been considerably diluted with water. The best results are obtained if phosphoric acid is used instead of sulfuric acid:

$$NaI+H_3PO_4=\underset{\text{Monosodium phosphate}}{NaH_2PO_4}+HI\uparrow.$$

To summarize: **The hydrogen halides are prepared by heating metallic halides with a non-volatile acid, such as H_2SO_4 or H_3PO_4;**

though concentrated H_2SO_4 may not be used for preparing HBr, nor even dilute H_2SO_4 for preparing HI (reasons in § 192).

191. Hydrolysis of the Phosphorus Halides.—When phosphorus burns in an atmosphere of chlorine gas it forms a liquid, PCl_3; or, if the chlorine is present in excess, a white solid, PCl_5. Both these substances are violently decomposed by water:

$$\underset{\text{Phosphorus trichloride}}{PCl_3} + 3H_2O = \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl;$$

$$\underset{\text{Phosphorus pentachloride}}{PCl_5} + 4H_2O = \underset{\text{Phosphoric acid}}{H_3PO_4} + 5HCl.$$

These are cases of **hydrolysis**—(§ 113).

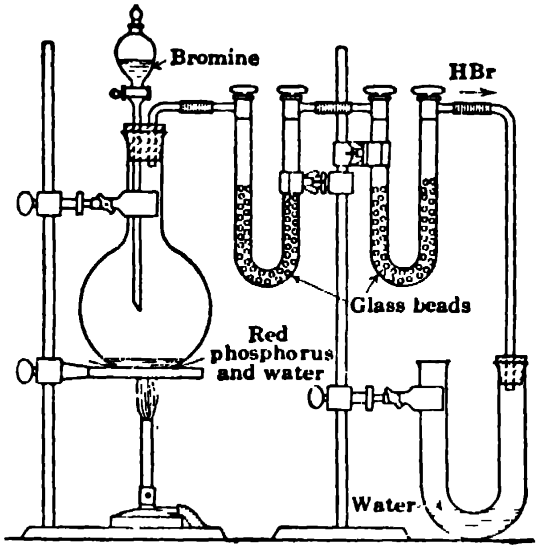


Fig. 57.—Preparation of hydrogen bromide.

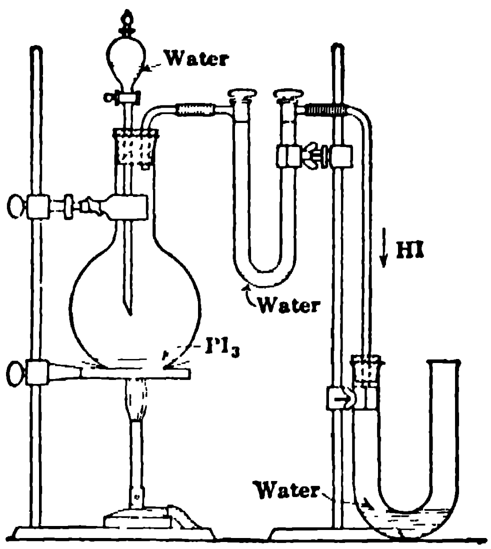


Fig. 58.—Preparation of hydrogen iodide.

Hydrobromic acid may similarly be prepared by hydrolysis of phosphorus tribromide.

We place some red phosphorus in a few cubic centimeters of water in the bottom of a flask (Fig. 57), and permit liquid bromine to drop upon it from a dropping funnel. The reaction takes place violently, the two elements uniting with a flash of light to form phosphorus tribromide, which is immediately decomposed by the water.

$$2P + 3Br_2 = 2PBr_3,$$
$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr \uparrow .$$

Hydriodic acid may be prepared by a similar method.

In this case we usually mix the red phosphorus with a large excess of iodine and heat the mixture cautiously in the bottom of the flask until the two elements have united to form PI_3. Water is then slowly added from the dropping funnel (Fig. 59). The stream of hydrogen iodide thus produced is freed from iodine vapor by being passed through a U-tube containing a few drops of water.

$$PI_3+I_2+4H_2O=H_3PO_4+5HI\uparrow.$$

To summarize: **The hydrogen halides may all be prepared by decomposing the phosphorus halides with water.**

192. Chemical Properties of the Hydrogen Halides.—Review §§ 179, 180. The most important properties of the hydrogen halides may be summarized as follows:

(1) **They react with bases (and combine directly with ammonia gas) to form salts:**

$$2HBr+Ca(OH)_2=\underset{\text{Calcium bromide}}{CaBr_2}+H_2O.$$

$$HI+NH_3=\underset{\text{Ammonium iodide}}{NH_4I}.$$

(2) **Their hydrogen is readily displaced by metals that lie above hydrogen in the electrochemical series.**

$$Zn+2HBr=ZnBr_2+H_2\uparrow.$$

Another example is the action of aluminum on hydrogen chloride (§ 179).

(3) **Their solutions decompose carbonates, sulfites, sulfides, and similar salts, liberating a gas.** Review § 114.

$$2HBr+CaCO_3=CaBr_2+H_2O+CO_2\uparrow;$$
$$2HCl+MgSO_3=MgCl_2+H_2O+SO_2\uparrow;$$
$$2HI+ZnS=ZnI_2+H_2S\uparrow.$$

The direction of such reactions is of course controlled by the circumstance that one of the products happens to be a gas, which is but slightly soluble and escapes. *Salts of acids less volatile than the hydrohalogen acids themselves would not be similarly decomposed.* (Give two examples.)

(4) **All the hydrohalogen acids, with the exception of hydrofluoric acid, can be oxidized, the product in each case being a halogen and water.** In illustration of this principle we have already noted the action of a number of different oxidizing agents on hydrochloric acid, forming chlorine and water (§ 180). **Hydro-**

bromic acid is still more readily oxidized, for even concentrated sulfuric acid is able to oxidize it. This is the reason why sulfuric acid has to be diluted before it can be used in the preparation of hydrobromic acid from metallic bromides (§ 190).

Hydriodic acid is so readily oxidized that even very feeble oxidizing agents are able to oxidize it. Thus concentrated hydriodic acid acquires a brownish tinge, on standing in the air, from liberation of iodine (write an equation showing that this change is due to the action of the oxygen of the air). But to say that hydriodic acid is easily oxidized by other substances is the same as saying that it is a *vigorous reducing agent.*

193. Secondary Reactions.— The student must strive to develop a vivid sense of the properties of substances, to predict whether they will react with each other, and is to what will be produced. But another point needs emphasis: **Sometimes the products of a reaction react with each other or with an excess of one of the original reactants, giving new products, in what is called a *secondary reaction.***

Consider the action of sulfuric acid on crystals of sodium bromide. We have already seen that fairly dilute sulfuric acid (sp. gr. 1.4) liberates hydrogen bromide, the reaction being one of double decomposition:

$$H_2SO_4 + NaBr = NaHSO_4 + HBr.$$

But hydrogen bromide is easily oxidized, and concentrated sulfuric acid is a vigorous oxidizing agent. The result is that if we employ sulfuric acid of a specific gravity much greater than we have indicated, its oxidizing properties come into play— part of the hydrogen bromide is unable to get away, but is oxidized to water and bromine.

$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2.$$

It might be presumed that we could get around the difficulty, and prevent this secondary reaction, by using just the quantity of sulfuric acid called for in the principal equation. But the first portion of the hydrogen bromide set free would even then find itself in the presence of an excess of sulfuric acid, and a part of it would be oxidized before it could escape.

The conclusion is then that **we must act upon bromides with sulfuric acid that has been somewhat diluted, if we wish to get hydrogen bromide uncontaminated by bromine**; or we must employ phosphoric acid, which will not oxidize any of the hydrogen halides.

The preceding reaction illustrates a fact we have pointed out several times before; that any given chemical formulation or equation is true under certain definite conditions, which the student is expected to be able to state. Under other conditions, an entirely different reaction may take place, or none at all.

194. Quantitative Reactions. Yield.– A balanced equation will enable one to calculate how much of a desired product may be obtained from a given weight of raw material only in case (1) the reaction is complete and (2) no secondary reactions occur. Furthermore (3) it is necessary that the desired product shall be separable from other products and from any unconsumed excess of reactants. If these three conditions are satisfied, we actually obtain from the reaction the quantity of the product that is calculated from the equation. The reaction is then said to be *quantitative*, or to have a yield of 100 per cent. Of course only such reactions may be employed in quantitative chemical analysis (§ 39) or in the determination of atomic weights. But many important commercial processes are carried out with yields not exceeding 80 per cent; and a few reactions used in the manufacture of dyestuffs have yields of hardly 10 per cent.

195. Physical Properties of the Halogens.- Turning now from a consideration of the hydrogen halides to the halogens themselves, uncombined with other elements, let us note again that the latter are all colored. But the **depth of color and density increase with increasing atomic weight.** Fluorine (at. wt. 19) is a yellowish gas; but iodine (at. wt. 127) at the other end of the list is a purplish-black solid. But the **chemical activity is found to decrease with increasing atomic weight.**

Summary:

	Fluorine.	*Chlorine.*	*Bromine.*	*Iodine.*
Atomic weight	19	35.46	79.92	126.92
Color	Pale yellow	Greenish-yellow	Dark red	Purplish-black
Physical state	Gas	Gas	Liquid	Solid
Solubility in water	Violent reaction, yielding HF and O_3	0.6 g. = 200 cc. in 100 cc.	3 g. = 1 cc. in 100 cc.	About 0.03 g. in 100 cc.
Chemical Activity	Greatest←———————————————Least			

197. Preparation of the Halogens by Oxidation of the Hydrohalogen Acids.—The halogen elements are commonly prepared in the laboratory **by oxidizing the hydrohalogen acids.** But **fluorine** cannot thus be prepared, for hydrofluoric acid cannot be oxidized by any known oxidizing agent. We have already seen that any one of the more vigorous oxidizing agents will oxidize hydrochloric acid, forming water and **chlorine** (§ 180).

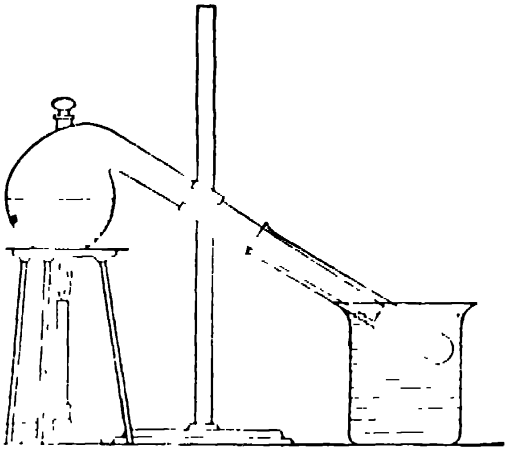


FIG. 59.—Preparation of bromine.

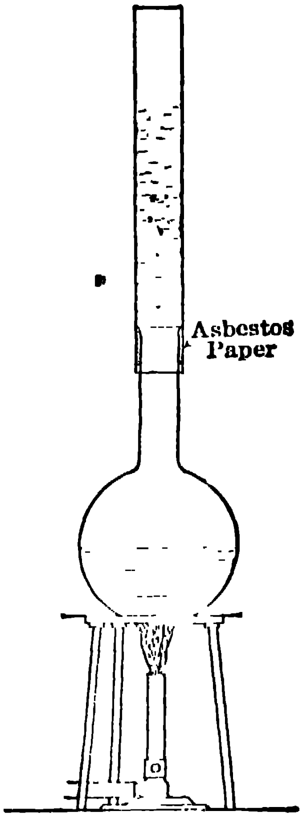


FIG. 60.—Preparation of iodine.

Bromine may be made by heating a mixture of manganese dioxide and sodium bromide with concentrated sulfuric acid in a glass-stoppered retort (Fig. 59). The hydrobromic acid produced by the action of the acid on the salt

$$NaBr + H_2SO_4 = NaHSO_4 + HBr,$$

is immediately oxidized,

$$2HBr + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + Br_2.$$

The bromine formed distils over, and condenses as a dark red liquid in the receiver. Is this a complete reaction? Explain.

What salt of sodium will be formed if sulfuric acid is used in excess? Explain.

Iodine is similarly prepared by heating sodium iodide with sulfuric acid and manganese dioxide.

But in this case the receiver may conveniently take the form of a wide glass tube (Fig. 60). Vapors of iodine condense on the walls of this tube in beautiful purplish-black leaflets. This is *sublimation*—a process in which a solid passes directly into a vapor form, without first melting.

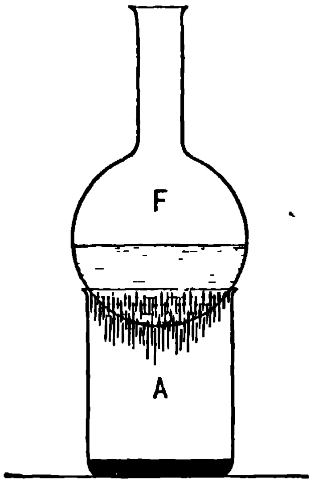


Fig. 61.—Purification of iodine by sublimation. Iodine crystals mixed with a little powdered potassium iodide, are heated in a beaker, and the vapors condensed on the bottom of a flask containing cold water.

197. Preparation of the Halogens by Electrolysis.—The preparation of fluorine by electrolysis is of scientific interest, because it is the method by which that element was first prepared. Its resemblance to hydrogen chloride very early led chemists to assume hydrogen fluoride to be a compound containing hydrogen, in combination with an undiscovered halogen. Davy, who had the honor of discovering a number of the metallic elements (§ 430), and several other experienced investigators made repeated attempts to oxidize hydrogen fluoride and thus obtain the free halogen. None of these efforts were successful. But in 1886 the distinguished French chemist, **Moissan, succeeded in preparing fluorine by electrolysis of a solution of potassium fluoride in liquefied hydrogen fluoride.** Under these conditions the hydrogen fluoride alone is decomposed, the potassium fluoride serving merely to make the liquid a conductor, as happens when sulfuric acid is added to water (§ 65).

$$2HF = \underset{\text{Cathode}}{H_2 \uparrow} + \underset{\text{Anode}}{F_2 \uparrow}.$$

The commercial preparation of **chlorine** by electrolysis is described in § 181.

When the brine from certain salt wells in Michigan and Southern Ohio is evaporated until a large part of the sodium chloride has crystallized out, the mother liquor (§ 97) is found to contain considerable amounts of sodium bromide. **Bromine** is prepared by electrolysis of these liquors:

$$2NaBr + 2H_2O \rightarrow 2NaOH + \underset{\text{Cathode}}{H_2 \uparrow} + \underset{\text{Anode}}{Br_2 \uparrow}.$$

198. Action of the Halogens on Other Elements.—The study of this section should be preceded by a review of the properties of chlorine (§§ 180, 182, 183, 184). We have previously noted that **the halogen elements become less and less active with increasing atomic weight.**

Thus fluorine combines vigorously with both metals and non-metals, even at very low temperatures. The only elements, in fact, that fail to form fluorides are the inert gases (§ 583) and oxygen. But iodine, at the other end of the list of halogens, reacts with mercury, hydrogen, and phosphorus only upon being heated, and fails to unite at all with certain other elements, such as silicon and carbon.

This regular **decrease in activity with increasing atomic weight** should be kept in mind while we examine the principal respects in which the halogens are chemically alike:

(1) **Direct union with metals.**

We may here recall the energetic union of chlorine with such metals as gold, copper, and antimony (§ 183). Bromine unites violently at room temperature with metallic sodium; and iodine vapors, when moderately heated, combine vigorously with mercury and other metals.

(2) **Direct union with non-metals.**

An example is the union of the halogens with phosphorus, already described as an intermediate step in the preparation of the hydrogen halides (§ 191). **Most non-metallic halides,** like the phosphorus halides, **are completely hydrolyzed by water.**

Write and balance equations for the hydrolysis of silicon tetrachloride, assuming the product to be orthosilicic acid, H_4SiO_4; and of phosphorus trifluoride, forming phosphorous acid and hydrofluoric acid.

(3) **Direct union with hydrogen.**

So active is *fluorine* that even when solidified by cooling to −250° C. it combines explosively with liquid hydrogen, to form hydrogen fluoride, even in the dark. This is one of the few known cases of chemical reactivity at the extremely low temperature of liquid hydrogen or even that of liquid air.

Chlorine and hydrogen will remain in contact indefinitely in the dark, without appreciable combination. In diffused light they combine slowly, and in bright sunlight explosively, to form hydrogen chloride.

Bromine and hydrogen can be made to unite to form hydrogen bromide. But the mixture must be heated to about 200° C., even in the sunlight; or it must be heated and passed over a catalytic agent, such as finely divided platinum.

Iodine vapor and hydrogen can be made to unite by passing them through a hot tube containing a catalytic agent. Even then the reaction is reversible and accordingly incomplete (§ 67);

$$H_2+I_2 \rightleftarrows 2HI.$$

199. The Halogens as Oxidizing Agents.—(*a*) In the reactions just discussed the halogens serve as **oxidizing agents,** since the other element, in each case, has its valence increased. Furthermore such salts as the ferrous, mercurous, and stannous halides can be oxidized by direct union with a further quantity of halogen, giving the corresponding ferric, mercuric, and stannic compounds:

$$2FeBr_2+Br_2=2FeBr_3;$$

$$2HgI+I_2=2HgI_2;$$

$$SnCl_2+Cl_2=SnCl_4.$$

Whenever the free halogens serve as oxidizing agents they are themselves reduced, decreasing in valence from 0 to −1.

Thus when sulfur dioxide gas is bubbled through a layer of bromine covered with a very little water, and contained in a tall cylinder, we have the reaction

$$SO_2+Br_2+2H_2O=H_2SO_4+2HBr.$$

This furnishes a very convenient method for the preparation of hydrogen bromide, which escapes from the cylinder in a steady stream, as soon as the layer of water at the top (to wash the gas) has become saturated.

Similarly when hydrogen sulfide gas is bubbled through water containing powdered iodine in suspension, hydriodic acid is formed, which may be decanted from the separated sulfur and separated by distillation.

$$H_2S+I_2=S+2HI.$$

200. Action of the Halogens on Compounds of Other Halogens. —If we arrange the halogens in the order of increasing atomic weight—F_2, Cl_2, Br_2, I_2—we find that **each halogen can displace**

any halogen of higher atomic weight from combination with hydrogen or metals.* Fluorine replaces all three of the others, chlorine replaces bromine and iodine, bromine replaces iodine.

$$F_2+2HCl=2HF+Cl_2,$$

$$Cl_2+MgBr_2=MgCl_2+Br_2.$$

(A commercial method for preparing bromine).

$$Br_2+2NaI=2NaBr+I_2.$$

$$Br_2+NaCl=\text{no action}.$$

201. Action of the Halogens on Hydrocarbons.—A **hydrocarbon** is an organic compound containing hydrogen and carbon only. **When a hydrocarbon is acted upon by chlorine or bromine a part or all of its hydrogen atoms are often replaced by the halogen.**

Thus if liquid bromine is added to powdered naphthalene (the substance used for moth-balls) a part of the hydrogen of the latter compound is replaced by bromine, even at room temperature.

$$C_{10}H_8+Br_2=\underset{\substack{\text{Monobrom}\\ \text{naphthalene}}}{C_{10}H_7Br}+HBr.$$

Reactions similar to this are of importance in the preparation of intermediate substances, to be used in the manufacture of dyes (§ 372). Most of the hydrobromic acid of commerce is a by-product of this reaction, which serves also as a convenient laboratory method for preparing dry hydrogen bromide gas.

202. Action of the Halogens on Water. Fluorine decomposes water explosively, giving hydrofluoric acid and ozonized oxygen:

$$3F_2+3H_2O=6HF+O_3.$$

Chlorine dissolves in water, then reacts slowly with it, until a mixture is obtained that contains unchanged chlorine in equilibrium with hypochlorous and hydrochloric acids (§ 184):

$$Cl_2+H_2O \rightleftarrows HCl+HClO.$$

---

* But it should be noted that this order of replacement of the halogens by each other may not hold for the oxygen compounds of the halogens. Thus iodine displaces chlorine when iodine vapors are passed over heated potassium chlorate.

Solutions of bromine are stable in the dark, but decompose slowly in the sunlight, forming hydrobromic acid and oxygen:

$$2Br_2+2H_2O \rightleftarrows 4HBr+O_2.$$

Iodine dissolves only very slightly in water, and is practically unaffected by it.

203. Action of the Halogens on the Caustic Alkalies.—The three less active halogens (Cl_2, Br_2, I_2) react with the **caustic alkalies** (i.e., the most active bases, § 107) forming **metallic halides, hypohalites, and water.** Special precautions must be taken to prevent the solutions from becoming heated during the course of the reaction:

$$Cl_2+2NaOH=NaCl+\underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaClO}+H_2O;$$

$$Br_2+2NaOH=NaBr+\underset{\substack{\text{Sodium}\\\text{hypobromite}}}{NaBrO}+H_2O;$$

$$I_2+2NaOH=NaI+\underset{\substack{\text{Sodium}\\\text{hypoiodite}}}{NaIO}+H_2O.$$

If the halogen is added to a hot solution of the alkali the hypohalite is converted into a mixture of halate and halide:

$$3NaClO \rightarrow 2NaCl+\underset{\substack{\text{Sodium}\\\text{chlorate}}}{NaClO_3},$$

$$3KIO \rightarrow 2KI+\underset{\substack{\text{Potassium}\\\text{iodate}}}{KIO_3}.$$

This conversion of the hypohalite into halate goes on slowly even in the cold. Hypochlorite solutions can therefore be preserved only a few days; while hypobromite and hypoiodite solutions are even less stable.

Note that these **oxy-halogen compounds** become more and more stable—less easily decomposed—with increasing content of oxygen:

$HF \rightleftarrows H_2F_2$	HCl	HBr	HI
....	$HClO$	$HBrO$	HIO
....	$HClO_2$	......	....
....	$HClO_3$	$HBrO_3$	HIO_3
....	$HClO_4$	......	HIO_4

Name the compounds listed in this table (§ 171). Write the names and formulas of their ammonium, ferrous, and ferric salts.

204. Bleaching Powder. The most important oxygen compound of the halogens is **bleaching powder,** made by absorbing chlorine in slaked lime, $Ca(OH)_2$:

$$Ca(OH)_2 + Cl_2 = \underset{\substack{\text{Bleaching}\\\text{powder}}}{CaCl(OCl)} + H_2O.$$

This substance, $CaCl(OCl)$, often incorrectly called "chloride of lime," is intermediate in composition between calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$. When acidified with a dilute acid, chlorine is liberated:

$$CaCl(OCl) + 2HCl = CaCl_2 + H_2O + Cl_2.$$

This property makes it valuable for bleaching (§ 185). About half a million tons of bleaching powder are still manufactured each year, though it is tending to be displaced by sodium hypochlorite and liquid chlorine.

Even the carbon dioxide of the air is able to decompose moist bleaching powder slowly, liberating hypochlorous acid. This breaks down, setting free **chlorine** monoxide, Cl_2O, which smells like chlorine:

$$\begin{array}{r} 2CaCl(OCl) + CO_2 + H_2O = CaCl_2 + CaCO_3 + 2HClO \\ \downarrow \quad \\ H_2O + Cl_2O. \end{array}$$

This reaction is the cause of the odor of fresh bleaching powder.

205. Hypochlorites.—Hypochlorites are prepared *on a laboratory scale* by the action of chlorine on a cold solution of a base or soluble carbonate (§ 184).

Write and balance equations for the preparation of potassium hypochlorite from caustic potash; and sodium hypochlorite from sodium carbonate.

Solutions of hypochlorites are **unstable,** forming chlorates and chlorides, slowly at room temperature, and more rapidly on warming:

$$3NaClO = NaClO_3 + 2NaCl.$$

Dilute solutions of hypochlorites on being acidified liberate hypochlorous acid, a powerful bleaching agent (§ 185). More concentrated solutions, on being acidified, yield *chlorine*:

$$NaClO + 2HCl = NaCl + H_2O + Cl_2.$$

During the Great War a hypochlorite solution known as Dakin's solution was used with great success in military surgery. It consisted of sodium hypochlorite and sodium chloride, usually prepared by action of chlorine on sodium carbonate, with addition of some boric acid. This fluid, used for irrigating infected wounds, not only saved thousands of lives, but restored many limbs to use, which under the older surgical procedure would have been permanently stiffened.

206. Chlorates and Perchlorates.—Potassium and sodium **chlorates** are prepared commercially by electrolysis of saturated warm solutions of potassium and sodium chlorides. Sodium or potassium hydroxide is formed at the cathode, while chlorine gas is liberated at the anode; but, instead of keeping these products apart, by means of an asbestos diaphragm (§ 181) the solution is stirred for the express purpose of bringing them together:

$$2KOH + Cl_2 = KCl + \underset{\text{Potassium hypochlorite}}{KOCl} + H_2O.$$

The hypochlorite thus formed is decomposed forming a chlorate, which precipitates.

$$3KClO = 2KCl + KClO_3 \downarrow .$$

If solid sodium or potassium chlorate is heated until it just melts, and then kept melted for some time, it loses about a third of its oxygen, and is converted into a mixture of chloride and **perchlorate.**

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Perchlorates are made commercially by electrolysis of concentrated solutions of chlorates.

Perchlorates are much more stable than the chlorates, in spite of their higher content of oxygen. But when strongly heated, especially in the presence of catalytic agents (§ 52) they lose all their oxygen, and are converted into chlorides.

Dry chlorates and perchlorates are powerful oxidizing agents. They must never be ground in a mortar with any easily oxidizable material, such as sugar, sulfur, or magnesium powder, or a violent explosion may result. This property enables potassium and sodium chlorates to be used in percussion caps for small arms ammunition, in matches, fireworks, and flashlight powders; and as oxidizing agents in the manufacture of certain dyes.

Dry chlorates, treated with concentrated sulfuric acid, form chlorine heptoxide, Cl_2O_7, which usually **explodes violently.** Never try this experiment with more than a very small pinch of the solid chlorate. In general, be aware of the **extreme danger** attending incautious work with chlorates and perchlorates.

207. Chloric Acid and Perchloric Acid.—A solution of chloric acid, $HClO_3$, may be obtained by acidifying a solution of a chlorate with a dilute acid. This may be concentrated to about 40 per cent $HClO_3$, by evaporation in a vacuum. But on further concentration the material is decomposed, forming perchloric acid and other products. Solutions of chloric acid are very vigorous oxidizing agents.

A solution of perchloric acid, $HClO_4$, obtained by acidifying a solution of a perchlorate, may be concentrated by distillation in a vacuum. The perchloric acid hydrate thus obtained, $HClO_4 \cdot H_2O$ is a colorless, oily liquid, which often explodes violently when brought in contact with easily oxidizable material. Somewhat diluted it loses its oxidizing properties, and becomes as hard to reduce as dilute sulfuric acid (§ 241). It is then perfectly safe, and an important reagent in analytical chemistry (§ 444).

208. Iodic Acid and Iodates.—Iodic acid is the most important of the oxygen compounds of bromine and iodine. It may be prepared by the direct oxidation of iodine with nitric acid:

$$3I_2+10HNO_3+4H_2O=6HIO_3 \cdot H_2O+10NO.$$

It is a crystalline solid, which is much more stable than chloric acid. Its salts, the *iodates*, are rather less readily decomposed by heat than the chlorates. We have already noticed (§ 192) that iodic acid oxidizes hydriodic acid, both compounds yielding iodine. This reaction is of some importance in analytical chemistry.

Iodine pentoxide, I_2O_5, the anhydride (§ 238) of iodic acid, is sometimes used in the laboratory, or in gas-masks, for absorbing carbon monoxide.

209. Uses of the Halogens and Halogen Compounds.—The principal mineral of **fluorine** is calcium fluoride, or **fluorspar,** CaF_2. This as its name implies, is used as a flux (§ 421) to make certain infusible substances melt or flow more easily when heated in a furnace. Another important mineral is **cryolite,** Na_3AlF_6, used in the preparation of metallic aluminum (§ 474). Although fluorine itself is but a chemical curiosity, many of its compounds have important uses. **All fluorides are intensely poisonous.** Lithium and sodium fluorides are used as a flux, for soldering aluminum. Solutions of sodium fluoride are used to impregnate wood, to preserve it from destruction by fungi. Other metallic fluorides are constituents of enamels, for coating metals. Hydrofluoric acid is used for etching glass.

The principal ingredient of glass is calcium silicate. The effect of the hydrofluoric acid is to form silicon fluoride, SiF_4, which is a gas, and escapes. Very roughly formulated:

$$CaSiO_3+6HF=CaF_2+SiF_4\uparrow+3H_2O.$$

Hydrofluoric acid is also used in the laboratory in the analysis of silicate rocks, which are insoluble in all the ordinary reagents, but are easily decomposed by heating with a mixture of sulfuric and hydrofluoric acids.

Refer to previous sections for the uses of **hydrochloric acid** (§ 187), **chlorine** (§ 187), bleaching powder (§ 204), hypochlorites (§ 205), and chlorates (§ 206).

Bromine (source, § 197) is used in the preparation of dyestuffs, and to a slight extent as a disinfectant. Bromides are used in medicine as heart depressants and nerve sedatives. Silver bromide emulsions are used for covering photographic plates and films (§ 545).

Most of the **iodine** of commerce occurs as an impurity, as sodium iodate and periodate, in the Chile saltpeter deposits of South America (§ 279). It is commonly reduced from this by sulfur dioxide. A solution of iodine in alcohol, called **tincture of iodine,** is an important antiseptic.

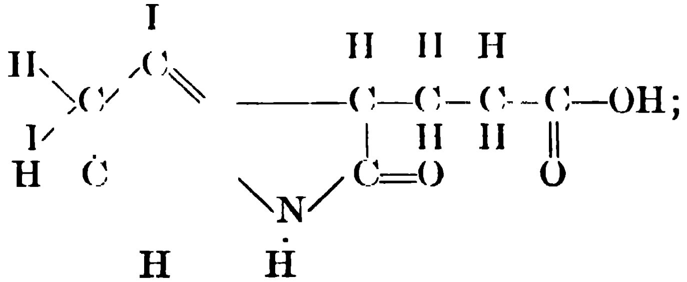
Other iodine compounds used as antiseptics are iodoform,

CHI_3, and iodole (C_4I_4NH). Hydriodic acid is used as a reducing agent in the preparation of many important organic compounds. **Silver iodide** is used in photography.

210. Thyroxin.—It has long been known that the animal body contains small amounts of chemically combined iodine, which is chiefly localized in the thyroid gland, near the base of the neck. Experience has moreover shown that iodine, in very small amounts, is a necessary ingredient of the diet (§ 391). Indeed, serious derangements of the health, of a kind now known to be due to a deficient supply of iodine, are common in certain communities in which the water supply and the soil (and consequently the crops produced locally) happen to be lacking in this element. Recently, in at least one such situation, arrangements have been made to add a definite small amount of sodium iodide to the water supply of an entire city, and "iodized" table salt (containing a trace of sodium iodide) is now on the market.

In the treatment of such clinical cases as have been recognized as being due to a deficiency of iodine, it has been found that the powdered, dried thyroid gland of the sheep or hog, or an extract of this gland, produces an immediate improvement. Thus it became evident that the thyroid gland contains or secretes some substance, the lack of which produces derangements known as cretinism (Fig. 62) and myxoedema. On the contrary, an excess of this substance may induce exophthalmic goiter. These facts, which have now been known for a long time, were a challenge to chemists to isolate and identify the substance which the thyroid gland secretes, then to determine its structural formula, and finally to synthesize it from simple and cheap materials.

The first of these problems was solved in 1914 by the efforts of Dr. E. C. Kendall and associates, of the Mayo Foundation. By extracting several tons of thyroid glands, they obtained a few grams of a soluble crystalline substance, which proved to have the formula, $C_{11}H_{10}O_3NI_3$, and which they named thyroxin. Continued research showed that it had the structural formula,



and that it had its effects, which, when a few milligrams were administered by intravenous injection, were identical with those previously obtained with much larger quantities of the dried thyroid gland.

The derangements due to deficiency of iodine (or, as we now know, to deficiency of the iodine compound, thyroxin) have been shown to be induced by the failure of certain chemical reactions within the body, which supply the needs of the body for energy (§389). Thyroxin serves as a catalyzer for these reactions, and it is now known that the traces of thyroxin which enter the blood stream from the thyroid gland are sufficient to account for more than 40 per cent of all the energy of the body, in health.

The effect of small doses of thyroxin, of a few milligrams each, at intervals of some weeks, over a period of a number of months, is to maintain the production of energy at a nearly normal rate, and often produces results nothing short of marvelous (Fig. 62). In addition, traces of thyroxin have an interesting catalytic effect on the metamorphosis of tadpoles, so that miniature frogs result in a fraction of the time that would be needed for the growth and development of normal frogs from the tadpole stage. This effect has sometimes been put to use in measuring the physiological effect of thyroid preparations of unknown strength. At the present time (1925) thyroxin itself has not been synthesized, but a number of substances of similar structural formulas have been prepared and their properties have been studied. Thus, we may presently arrive at an understanding of how thyroxin itself produces its remarkable effects.

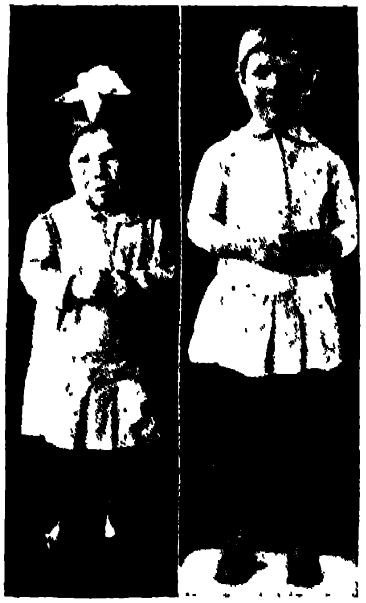
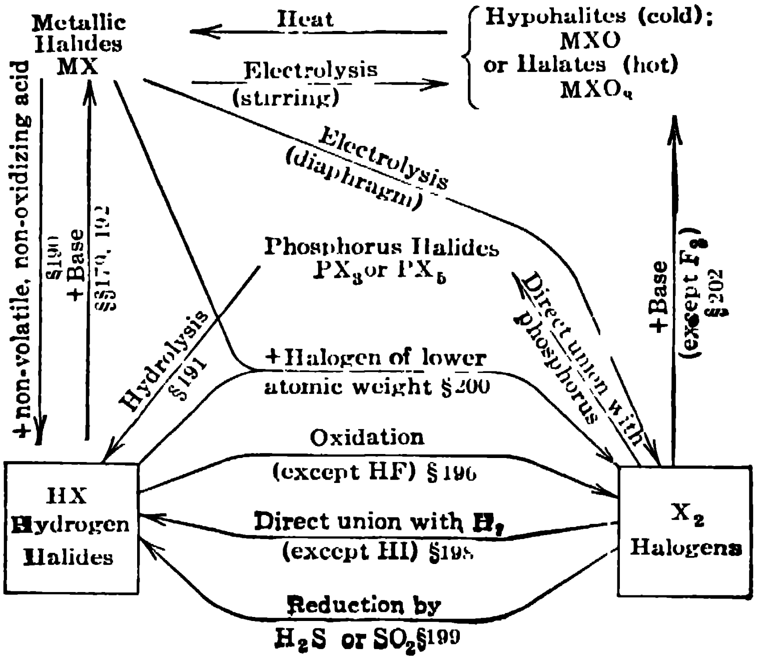


FIG. 62.—Effect of thyroxin on the growth of a cretinous child. The same child, in the same dress, before and after receiving thyroxin for one year. Increase in height, 6 inches.

211. Graphical Summary.—(Letting M represent a metal and X any halogen.)


Metallic Halides MX
Heat
Electrolysis (stirring)
Hypohalites (cold); MXO or Halates (hot) MXO₃
+non-volatile, non-oxidizing acid §190
+Base §§179, 192
Electrolysis (diaphragm)
Phosphorus Halides PX₃ or PX₅
Hydrolysis §191
Direct union with phosphorus
+Base (except F₂) §202
+Halogen of lower atomic weight §200
Oxidation (except HF) §196
Direct union with H₂ (except HI) §198
Reduction by H₂S or SO₂ §199
HX Hydrogen Halides
X₂ Halogens

	Hydrogen Halides	Halogens
Action on hydrogen	none	direct union
Action on metals	hydrogen displaced	direct union
Action on non-metals	none	direct union
Action on water	dissolve	react (except I_2)
Action on bases	form halides	form halides and hypohalites (cold); or halides and halates (hot); except F_2
Oxidizing or reducing	reducing (except HF)	oxidizing
Action on halides	none	any given halogen displaces any other of higher atomic weight

EXERCISES

1. Predict the physical properties and reactions with metals, water, alkalies, and sodium iodide of an undiscovered halogen of atomic weight 219.

2. The same for an imaginary halogen of atomic weight 3.

3. From the general properties of the halogens, complete the following formulations, and name the compounds formed:

$SbBr_3 + Br_2 \rightarrow$
$Al + HBr \rightarrow$
$NaOH$ (cold solution) $+ Br_2 \rightarrow$
$KMnO_4 + HI \rightarrow$
$Ca(OH)_2$ (hot solution) $+ I_2 \rightarrow$
$MnO_2 + HBr \rightarrow$
$CaBr_2 + Cl_2 \rightarrow$
$SiO_2 + HF \rightarrow$

4. Explain why hydrogen bromide cannot be prepared by the action of concentrated sulfuric acid on potassium bromide. Write and balance equations for two successful methods for preparing hydrogen bromide, and one for preparing bromine, from potassium bromide.

CHAPTER XVI

REACTION VELOCITY AND CHEMICAL EQUILIBRIUM

Many chemical reactions are *instantaneous*. Thus when hydrochloric acid is added to sodium hydroxide, the reaction becomes complete in a fraction of a second. But many other reactions proceed very slowly, requiring months or years to become complete or to reach a condition of equilibrium. This matter of *reaction velocity* is of great importance, as determining whether a given chemical change can be carried on at a practically useful rate. Moreover it determines whether a chemical change shall become reasonably complete, or whether it shall remain so incomplete as to be quite valueless.

212. Factors Determining the Speed of Reactions.

—The speed at which chemical reactions proceed is chiefly determined by the following circumstances:

1. **The nature of the reagents.** Review § 72. Those that are most active react most rapidly, under given conditions.

2. **Their state of subdivision.** Chemical reactions between different substances can, of course, take place only at the surfaces at which they come into contact. When two substances are finely divided and intimately mixed they present more surface to each other, and thus react more rapidly than coarser material. This is admitted whenever we are advised to chew our food well.

Solutions react even more rapidly, for here the process of subdivision has been continued right down to the individual molecules of the dissolved substance. The finely powdered constituents of baking powder, if kept dry, will remain in contact with each other for years, without noteworthy change. But the moment water is added there is a violent reaction, liberating carbon dioxide gas.

3. **The temperature.** Almost without exception, reactions proceed more rapidly as the temperature is increased. The housewife keeps milk in a refrigerator in order that the velocity of the reactions that result in the souring of milk may be retarded; but she sets dough in a warm place, to increase the velocity of the reactions carried out by the yeast, producing carbon dioxide, to cause the dough to rise. Every amateur understands that the length of time that it takes to develop a photographic film depends on the temperature of the developing solution.

Many reactions are roughly doubled in velocity by each rise of ten degrees in temperature.

But though a reaction is probably always made more rapid by a *slight* increase of temperature, (*a*) it may sometimes be less complete; or (*b*) secondary reactions (§ 193) may appear at the higher temperature and decrease the yield; or (*c*) too high a temperature may at times destroy or restrain some living organism, or catalyzer, responsible for the progress of the reaction, and give a velocity actually smaller than that which is obtained at a more moderate temperature.

4. **The nature of the solvent or the presence of small amounts of other substances.** Substances that increase the speed of a reaction, without themselves suffering any *permanent chemical change*, are called **catalyzers.** Those that decrease its speed are called negative catalyzers or **retarders.**

5. **The concentration of each reactant, i.e., the number of molecules in unit volume.** This applies only to reactions in which the reactants are present in a **homogeneous mixture or true solution**—gaseous, liquid, or solid. But when this is the case, doubling the concentration of any reactant doubles or more than doubles the reaction velocity. We shall discuss this principle in detail in what follows (§ 214).

6. **Many reactions are accelerated by light—photochemical reactions.** Examples are the decomposition of hypochlorous acid (§ 184); the union of chlorine and hydrogen (§ 183 1); and the synthesis of starch in the leaves of green plants (photosynthesis, § 325).

213. A Lecture Experiment on Reaction Velocity.—To illustrate the effect of temperature and concentration on reaction velocity, let us consider the reduction of iodic acid to hydriodic acid by sulfurous acid:

(*a*) $HIO_3+3H_2SO_3=HI+3H_2SO_4$.

Mix dilute solutions of sulfurous acid and starch. Add an excess of dilute iodic acid, shake, and pour into a tall cylinder. There is no visible result for one or two minutes. Then the liquid suddenly turns blue! This indicates that the given reaction has become complete, and has been succeeded by another, which liberates iodine.

A more complete explanation is that reaction (*a*) is accompanied by two others, *one producing, the other consuming iodine*:

(*b*) $HIO_3+5HI=3H_2O+3I_2$.

(*c*) $I_2+H_2SO_3+H_2O=H_2SO_4+HI$.

No iodine can accumulate in the solution so long as (*b*) and (*c*) are going on together. But the moment (*a*) becomes complete, by exhaustion of the H_2SO_3, (*c*) must necessarily cease as well. Then (*b*) keeps on going, liberating enough iodine in the next fraction of a second to color the starch blue.

Suitable proportions for this experiment are: (*A*) 500 cc. water, a little starch solution, 15 cc saturated solution of SO_2; (*B*) 500 cc. water, 10 cc. 5 per cent solution of HIO_3.

If the experiment is repeated, with the same conditions as before, except that the upper part of the liquid in the cylinder is warmed with an electric heating coil, it is found that this upper layer turns blue first. This shows the increase of reaction velocity with increasing temperature.

Finally, if twice as much iodic acid is taken, the doubled concentration means doubled reaction velocity, and brings the given reaction to completion in about half the former time.

214. How the Molecular Theory Explains the Effect of Increased Concentration.—The Molecular Theory (§ 88) gives a very simple explanation of the effect of increased concentration in increasing the velocity of chemical reactions. Consider a mixture of chlorine and hydrogen gases, contained within a glass vessel, and slowly combining to form hydrogen chloride under the influence of diffused sunlight (§ 160):

$$H_2+Cl_2 \rightarrow 2HCl.$$

We think of the molecules of hydrogen and chlorine as being in rapid motion, in all conceivable directions, with all conceivable velocities, throughout the space occupied by the mixture of gases. At the given temperature we may assume that a definite percentage of all the collisions of molecules of hydrogen with molecules of chlorine results in chemical union. Anything, then, that increases the number of such collisions will increase the velocity of the reaction proportionately.

Doubling the concentration of the hydrogen, in grams per liter, by Avogadro's principle, means doubling the number of molecules of that gas confined in the given space; and this in turn means that any given molecule of *chlorine* will have twice as great a chance of colliding with a molecule of hydrogen as it had before. Doubling the concentration of hydrogen therefore doubles the speed of the reaction. It is plain that doubling the concentration of the chlorine would have the same effect.

It is now easy to see what will be the effect of increasing the concentration of *both* the reacting substances. Let us imagine the concentration of the hydrogen to be increased three-fold and that of the chlorine four-fold. There are now three times as many hydrogen molecules in the given space as before; and each of these, in its haphazard wanderings, has four times the former chance of meeting a molecule of chlorine. The velocity of the reaction has accordingly been increased twelve-fold.

Thus we conclude that **whenever reacting molecules combine one to one, the velocity of the reaction is proportional to the product of concentrations of the reacting substances.**

This is a simplified form of what is called the **Law of Mass Action.** Notice that it has nothing to do with the *total mass or weight* of the reacting substances, but only with their concentration, or *mass per unit volume.* Notice, furthermore, that **the rule as stated above applies only when the reacting molecules combine one to one.** In such a case as the union of two molecules of hydrogen with one of oxygen to make water, the situation is a little more complicated—the speed of the reaction being proportional to the *square* of the concentration of the hydrogen.

1. A vessel contains equivalent quantities (§ 115) of hydrogen and iodine vapor. How does the speed of the reaction,

$$H_2+I_2 \longrightarrow 2HI,$$

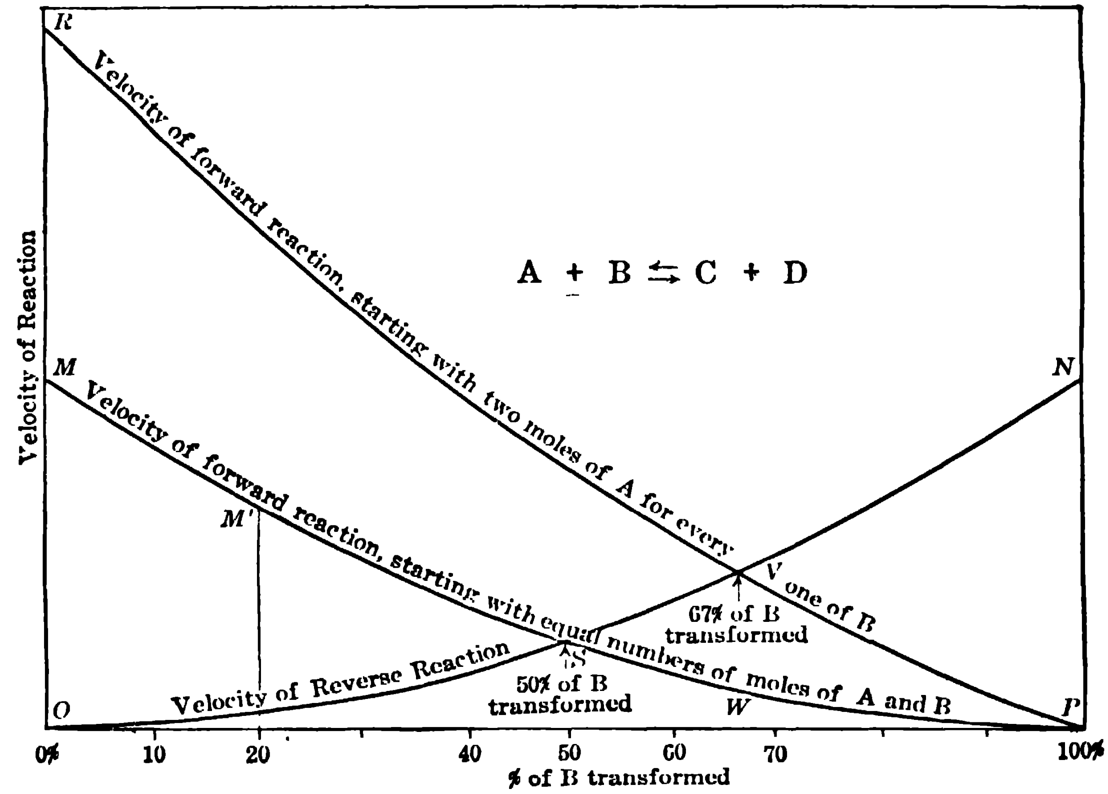
at first compare with its speed after three-fourths of each reactant have been consumed?

2. Compare the rate of combination of hydrogen and iodine, if the vessel contains one *mole* of each, with the rate if it contains 10.08 *grams* of hydrogen and 126.92 *grams* of iodine *vapor.*

215. Reactions Slow up as They Approach Completion.—The Law of Mass Action gives us the reaction rate only *at the particular instant* at which the concentrations have the values stated. After the reaction has proceeded for a little while, the concentrations of the reacting substances will be somewhat less and the reaction rate will have fallen off correspondingly. A mixture containing 3 gram-molecules of hydrogen and 4 gram-molecules of chlorine will combine in diffused sunlight just *twelve times as fast* as hydrogen and chlorine in a mixture containing but 1 gram-molecule of each in the given volume. But when two-thirds of the hydrogen has combined there will remain but 1 gram-molecule of hydrogen and 2 gram-molecules of chlorine. The reaction rate will then

be only *twice* what it would be in a mixture containing 1 gram-molecule of each in the same volume, or one-sixth of what it was at first. Thus reactions proceed more and more slowly as they become more and more nearly complete.

This is a little like the slowing down of a train as it approaches a station. But it is worth remarking that if the speed of the train were decreased proportionately to its nearness to the station it would take forever to arrive; for as it approached infinitely close it would move with infinite slowness. Thus a chemical reaction proceeding according to the law of mass action can never become *entirely* complete. But it will become as nearly complete as we may desire if we wait long enough—provided it does not first reach a condition in which the reverse reaction proceeds at the same rate (equilibrium).



In practice a reaction is considered as being complete when it has made a reasonable approach to completion—say when 99.9 per cent of one of the reactants has been consumed. By waiting a sufficient time, most of the so-called complete reactions ($2H_2+O_2 \rightarrow 2H_2O$) become even more nearly complete than this; while the so-called incomplete reactions ($H_2+I_2 \rightleftarrows 2HI$) come to an apparent standstill, due to an equilibrium between opposing reactions, leaving from a few tenths of a per cent to many per cent of the original reactants still unconsumed.

216. Equilibrium a Balancing of Reaction Velocities.—Let us consider two substances, A and B, which react to give two other substances, C and D, the reaction being incomplete because reversible:

$$A+B \rightleftarrows C+D.$$

The situation after various intervals of time is shown in the above diagram. *In the beginning, let A and B each be present in a concentration of one mole per liter.* The left to right reaction starts out with a velocity that is represented by the length of the line OM. But as the reaction proceeds the concentrations of the reactants become less and less, hence the velocity of the reaction falls off. We therefore get a downward sloping curve, *MM′S*, which represents the decreasing velocity as more and more of A and B are transformed.

But as soon as this *forward reaction* has proceeded for a moment, a measureable amount of the products C and D, will have been formed. These will then begin to react with each other to give back A and B. This *reverse reaction* will at first take place only very slowly, for C and D are at first present in only very small concentrations. Nevertheless, as time goes by, more and more of C and D come into being as a result of the forward reaction. The reverse reaction accordingly increases in velocity, as shown by the rising curve, *OSN*. After a little while the velocities of the forward and reverse reactions become equal; i.e., the two curves cross at some point, *S*. This represents a condition of equilibrium.

If we had begun with a mixture of C and D, instead of with one of A and B, the reverse reaction would have started off a velocity represented by *PN*. This velocity would have fallen off from moment to moment, as represented by the descending curve *NVS*, traced backward from the right. The other reaction would meanwhile have been increasing in velocity, as represented by the rising curve, *PWS*. The two curves cross at the same point, *S*, as before.

The diagram thus illustrates an important principle: **We cannot change the concentration of any substance in an equilibrium mixture by changing the direction of approach to equilibrium.**

Thus if hydrogen iodide is heated in a closed tube at 500° C., it is 24 per cent decomposed into hydrogen and iodine:

$$\underset{\text{76 per cent}}{2\text{HI}} \rightleftarrows \underbrace{\text{H}_2+\text{I}_2.}_{\text{24 per cent}}$$

But by heating equal volumes of hydrogen and iodine together at 500° C., 76 per cent of them combine to form hydrogen iodide, leaving 24 per cent uncombined, no matter how long the heating is continued.

Notice furthermore that **the addition of a catalytic agent never causes a reaction to become more complete, but merely enables the former equilibrium point to be reached more quickly.**

217. Effect of an Excess of One Reactant on Equilibrium.—In the reaction represented by the preceding diagram, let the substances A and B be mixed as before, but with the concentration of A doubled. What effect will this have on the amount of B that is transformed before equilibrium is reached?

Evidently doubling the concentration of A doubles the velocity with which the reaction starts off from left to right. As the reaction proceeds the concentrations of both A and B decrease, and the velocity of the reaction falls off, as represented by the descending line *RVP*.

But it is apparent that the velocity of the reverse reaction is not changed by the increased concentration of A. Its value from moment to moment is still represented by the ascending line *OSVN*. The two curves now cross at the point *V*, which represents a new point of equilibrium.

This illustrates a general principle: **An incomplete reaction may be made to take place more completely by adding an excess of any one of the reactants.**

But we may note that doubling the concentration of A does not double the amount of B transformed, but increases it only by a few per cent—from 50 per cent to 67 per cent in the example just considered, *in which C and D are assumed to have the same chemical activity as A and B.* When the quantity of C and D in the final equilibrium mixture is thus increased we commonly say that the equilibrium has been **shifted toward the right.**

218. Energy Changes in Chemical Reactions.—We have already noticed many cases of chemical reactions which liberate considerable amounts of energy, in the form of *heat* or *light*. A dry-cell or a storage battery is an example of a set of chemical reactions liberating *electrical energy*. Many other reactions absorb energy—electrical energy, for example in the preparation of chlorine and caustic soda by electrolysis of a solution of common salt (§ 181; or heat energy in decomposing hydrogen iodide into its elements (close of § 216).

Very often the quantity of energy released in a reaction is of more practical importance than the nature of the products formed. Thus we are interested in knowing that so many calories of heat energy are released when we burn a pound of coal. But the carbon dioxide and water vapor produced in the process concern us so little that we discard them by way of the chimney. We also need to remember that energy costs money; and when a reaction consumes energy it is often the amount consumed that determines whether the process can be made to pay a profit, if carried out on a commercial scale.

Chemists are in the habit of keeping track of the energy consumed or released in chemical reactions by what are called **thermochemical equations.** Thus,

$$2H_2+O_2=2H_2O\ (\text{liq.})+138{,}000\ \text{cals.},$$

indicates that when hydrogen is burned, and the water condensed to a liquid, there are 138,000 calories of heat liberated for every two moles (=36 g.) of water formed.

To reverse this reaction, and decompose two molecules of water into hydrogen and oxygen, this same amount of heat—or an equivalent amount of electrical energy—needs to be absorbed. If this were not the case—if less energy, for example, were needed to decompose water than is liberated by the recombination of its constituents—we should be able to create energy indefinitely, in violation of the Principle of Conservation of Energy (§6) by alternately decomposing water in an electrolytic apparatus, and recombining the products in an oxy-hydrogen blowpipe.

This illustrates a general principle: **The heat evolved in a given reaction**—for a given quantity of material transformed—**is always equal to the heat absorbed in the reverse reaction.**

219. Effect of Temperature on Equilibrium.—**If a reaction is reversible, both the forward and reverse reactions increase in velocity with increasing temperature** (§ 212). But the increase in temperature is usually more favorable to one of the two opposing reactions than to the other, and consequently changes the proportions in which the reacting substances are present when equilibrium is reached.

When two opposing reactions have reached a condition of equilibrium, the reaction that absorbs heat is made more nearly complete by raising the temperature; the reaction that liberates heat is made more nearly complete by lowering the temperature. This is Van't Hoff's Principle.

Thus, in the reaction,

$$2H_2+O_2 \rightleftarrows 2H_2O\ (\text{vapor})+116{,}600\ \text{cals.},$$

a high temperature makes the *right to left* reaction more complete. This means that water is slightly decomposed into its elements at high temperatures, and the more completely the higher the temperature. Experiments have given the following results:

° Abs.	*Per Cent Dissociated*
1500	0.02
1700	0.10
2155	1.18
2257	1.77

3. In which of the following reactions is direct union (§ 129) made more complete, and in which less complete by an increase in temperature? (A negative sign means heat absorbed in the left to right reaction.)

$$N_2+3H_2 \rightleftarrows 2NH_3+24{,}000 \text{ cals.}$$

$$C+S_2 \rightleftarrows CS_2 \text{ (vapor)} - 25{,}400 \text{ cals.}$$

$$C+O_2 \rightleftarrows CO_2+97{,}000 \text{ cals.}$$

$$N_2+O_2 \rightleftarrows 2NO-43{,}200 \text{ cals.}$$

Further applications in § 229.

220. Extremely Slow Reactions.—But we must be sure to note that **Van't Hoff's Principle applies only to systems of reacting substances that are already in equilibrium at the time the change in temperature takes place.**

Thus hydrogen and oxygen gases will remain in contact with each other indefinitely at room temperature, without anything happening. But if the temperature is raised, by passing an electric spark, violent combination takes place, forming water, and liberating heat. It looks as if an increase in temperature had favored a reaction liberating heat, in violation of Van't Hoff's Principle. The trouble is that **hydrogen and oxygen are not really in equilibrium with water vapor at room temperature,** and Van't Hoff's Principle cannot apply. We have rather a case of a reaction that is still proceeding toward equilibrium, at room temperatures, though at an **immeasurably slow rate.**

It is easy to distinguish equilibrium from extreme slowness of reaction rate. **In true equilibrium, any small decrease of temperature will always reverse the effect produced by a small increase of temperature.** But if hydrogen and oxygen are made to combine by raising the temperature, we find that lowering the temperature will not cause the water to decompose again, into hydrogen and oxygen. This is therefore not equilibrium.

221. The Principle of Le Chatelier.—This matter of **equilibrium** has important applications that extend far beyond the confines of chemistry. Not only do we have *chemical equilibrium,* between opposing reactions, but *mechanical equilibrium,* when a body is in a state of rest or frictionless uniform motion, under the influence of balanced forces. A saturated solution is a case of *molecular equilibrium,* molecules of crystalline salt entering the solution as fast as other molecules leave it, to come out again upon the surface of the crystals. The organs of the body, in health, are in *physiological equilibrium,* with respect to absorption and secretion. At some risk of exaggerating analogies we might discover further illustrations in the fields of biology or psychology, or even in political science.

But, dissimilar as are these applications, there is, remarkably enough, a general governing principle: **Systems in equilibrium change only with changing external conditions;** * **and then only in a way which tends to restore the original conditions.** This is the **Principle of Le Chatelier, sometimes called the Principle of Mobile Equilibrium,** one of the most far-reaching generalizations in the whole field of science.

Thus, in a reversible chemical reaction, an increase of temperature favors the reaction which *absorbs* heat, namely a change within the system that tends to restore the original temperature. Thus Van't Hoff's Principle is seen to be a special case of the Principle of Le Chatelier.

Again, in a reversible chemical reaction between gases, an *increase* of pressure will cause a reaction to take place in the direction which will *decrease the number of molecules in unit volume,* and thus tend to restore the original pressure. This, in the formation of ammonia from nitrogen and hydrogen

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

is the *left to right* reaction, for four molecules of nitrogen and hydrogen here disappear, for every two molecules of ammonia that are formed, leaving a net decrease of two molecules.

Conversely, a *decrease* of pressure will favor the dissociation (§ 157) of ammonia into hydrogen and nitrogen, for this takes place with an *increase* in the total number of molecules, and consequent tendency to restore the original pressure.

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* By *external conditions* we mean such conditions as temperature, pressure, or electrical charge—the things that determine the amount of *energy* contained in the system.

4. Which of the following reactions become most complete from left to right at high pressures, which at low pressures, and which are unaffected by a change in pressure:

$$2H_2+O_2 \rightleftarrows 2H_2O \text{ (vapor)};$$

$$H_2+I_2 \rightleftarrows 2HI;$$

$$N_2O_4 \rightleftarrows 2NO_2;$$

$$CO_2+H_2 \rightleftarrows CO+H_2O?$$

It will be noted that the preceding examples all concern reactions between *gases*.

The degree of completeness of reactions between solid or dissolved substances is hardly affected by change of pressure, for solids and liquids are but slightly compressible.

222. Other Illustrations of the Principle of Le Chatelier.— It may help us to fix this important principle in mind if we consider a few illustrations other than those afforded by reversible chemical reactions:

1. When liquid water in equilibrium with water vapor is heated, a part evaporates, absorbing heat, thus tending to restore the original temperature.

2. When a snowball is squeezed it is compacted into ice. The explanation is that some of the snow particles melt as the pressure is applied; for in so doing they tend to *relieve* the pressure, since the water formed by the melting occupies a smaller volume than the crystals of snow. But when the pressure is finally removed the reverse process takes place; the water that has been formed freezes again, and binds the remaining snow particles together into a solid mass.

But a substance like sulfur, which *increases* in volume when melted, can never be made to melt by pressure alone.

3. Any salt that *absorbs* heat when dissolving in a saturated solution, becomes more soluble as the temperature is *raised*. For in dissolving it tends to restore the original temperature.

Since most salts become more soluble with increasing temperature (§ 126), it is evident that **most salts dissolve in saturated solutions with absorption of heat.** But very many salts e.g., anhydrous $CaCl_2$, dissolve in *pure water* with liberation of heat.

4. When a junction of two dissimilar metals is *heated* an electric current is set up, which flows in such a direction that the junction

tends to be *cooled*. But if the junction is placed in ice, a current is set up in the opposite direction, and tends to *heat* the junction.

5. On closing an electric circuit containing a coil of wire, the current does not instantly reach its full strength; for it is opposed by what is called the *self-inductance* of the circuit, which tends to restore the original conditions, and prevent the current from flowing.

Conversely, when the circuit is opened, the current does not die away immediately, for self-inductance tends to keep it flowing, and a spark usually leaps across the gap caused by opening the switch.

6. When an animal is given an intravenous injection of a bacterial *toxin*, it reacts against the latter, and tends to restore the original conditions, by building up an *anti-toxin*. The animal is then found to be in a better condition to resist a second dose of toxin. It has acquired a certain degree of *immunity*.

223. Summary.

Reaction Velocity.

Greatest when reactants are very active chemically. May be increased—

1. By increasing fineness of subdivision (therefore greatest in solution). § 212.
2. By increasing temperature. §§ 212, 213.
3. By increasing concentrations of reactants. (Is proportional to the product of the concentrations of reactants, when molecules combine one to one - *Law of Mass Action.*) § 214.
4. By presence of a catalyzer (often).
5. By action of light (often).

Equilibrium.

A condition of balance between opposing forces or processes. § 40.

Molecular equilibrium. § 123.

Chemical equilibrium.

1. Defined as a state attained when two reactions, in opposite directions, have equal velocities. § 216.
2. Distinction from slow rate of reaction. (In true equilibrium the effect produced by a slight rise of temperature is exactly reversed by lowering the temperature.) § 220.
3. May be disturbed, and one of the two opposing reactions made more complete.
   - (*a*) By adding an excess of any reactant (equilibrium displaced toward right or left). § 217.
   - (*b*) By changing temperature.
     (Increasing temperature when the reaction to be favored absorbs heat; decreasing temperature when it evolves heat.)
     (Principle of Van't Hoff.) § 219.

(*c*) By changing pressure – for reactions between gases.
(Increasing pressure when reaction to be favored results in a decrease of pressure; decreasing pressure when it results in an increase of pressure.)
(An illustration of Principle of Le Chatelier—which includes that of Van't Hoff.) §§ 221, 222.

EXERCISES

1. Review the questions of §§ 214–221.

2. Under what four conditions does double decomposition commonly become complete? Illustrate.

3. Assuming that gasoline has the average formula C_6H_{14}, write and balance an equation for its complete combustion to form water vapor and carbon dioxide. Apply the principle of Le Chatelier to determine whether gasoline vapor burns more or less completely when highly compressed than it does under atmospheric pressure.

4. In spite of the result contained in the preceding problem, why is the mixture of air and gasoline vapor in an automobile engine always compressed before ignition?

5. Tell which of the following reactions are made more complete by an increase in pressure, and why.

Direct union of hydrogen and chlorine to form hydrogen chloride.

Union of sulfur dioxide gas with oxygen to form sulfur trioxide vapor (SO_3).

Decomposition of phosphorus pentachloride vapor (PCl_5) into phosphorus trichloride vapor (PCl_3) and chlorine.

6. Under what circumstances would a slight change in temperature have no effect on the degree of completeness of a reaction?

7. A quantity of air enclosed in an air-tight vessel, and exposed to a silent electric discharge (§ 33) never comes to contain more than two or three per cent of ozone, no matter how long the discharge continues. Do you think it might be possible to improve the yield by the use of a catalytic agent? Why or why not?

8. By what practical means can the dissociation of molecules of sulfur vapor of the formula S_8 into molecules of the formula S_2 be decreased, without changing the temperature?

CHAPTER XVII

SULFUR AND HYDROGEN SULFIDE *

Sulfur is of interest as one of the ten or twelve elements necessary for the life and growth of plants and animals. It makes up but a mere trace of the crust of the earth; yet there are in most parts of the world enormous deposits both of sulfur compounds and of the element itself. Sulfur is one of the cheapest of raw materials, and one of the most useful—the very cornerstone of the great chemical industries. Directly or indirectly, there is hardly a manufactured article, from automobiles to zinc paints, that has not met sulfur in its preparation.

224. Occurrence of Sulfur Compounds in Nature. Many of the most important metals are derived from sulfide ores. Zinc sulfide (or *zinc blende*, ZnS) and lead sulfide (or *galena*, PbS) are worth remembering as the most important sources of these two metals. Copper pyrites (or *chalcopyrite*, $CuFeS_2$) is an important ore of copper. The most important iron sulfide (*pyrite*, FeS_2) is of no use as an ore of iron, but until recently has been the chief raw material for the manufacture of sulfuric acid.

Notice that pyrite is a combination of ferrous sulfide, FeS, with an extra atom of sulfur; whence it is sometimes given the structural formula, $Fe = S - S$ (§ 142).

The most plentiful mineral containing both sulfur and oxygen is calcium sulfate (or gypsum, $CaSO_4 \cdot 2H_2O$). This is used for the preparation of plaster-of-Paris and Keene's cement (§ 453). Barium sulfate ($BaSO_4$) is mined on a large scale for the manufacture of cheap white paint, and for giving weight to silk fabrics. It is the principal source of the barium salts used in the chemical industries (§ 469).

225. Native Sulfur.—Sulfur occurs free or native (i.e., uncombined with other elements) in most volcanic regions of the world—Sicily, Italy, Japan, and South America. The Sicilian deposits until recently were the most important source of supply. From thence came most of the sulfur used by the European nations for the manufacture of gunpowder, in their almost incessant wars, from the introduction of firearms five hundred years ago down to the present day.

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* *To the Instructor*: This and the following chapter furnish a splendid opportunity for review and additional drill in the writing of formulas and equations.

But by far the largest deposits of sulfur in the world are those occurring in the United States, in Louisiana and Texas, which now supply over 80 per cent of the world's demand for this element.

Certain knolls appearing there above the surface of the surrounding level land are found to be underlaid with enormous deposits of sulfur at a depth of about 500 ft. These are now mined by the use of superheated water, introduced through pipes let down to the desired depth. The sulfur melts, and is then forced to the top by means of compressed air.

The sulfur produced in this way may amount to as much as 2000 tons a day from a single well; and individual deposits are known to contain as much as 10,000,000 tons. American sulfur is above 99.5 per cent pure, the most objectionable impurity being a trace of petroleum oil, which often prevents it from burning freely on stationary grates.

226. Allotropic Forms of Sulfur.—One of the interesting things about sulfur is its ability to exist in several different physical forms. Ordinary lump sulfur belongs to what is called the **orthorhombic** crystalline system, and forms blunt, irregular double pyramids. But if the sulfur is melted (a little above the boiling point of water) and allowed to cool, it forms long **monoclinic** needles. The existence of different crystalline forms of the same element is of course due to the possibility of arranging its atoms in two or more different space-patterns (§ 30) in building up the crystal lattice.

Liquid sulfur also exists in two different physical forms. Just above its melting point it is a pale yellow liquid, almost as fluid as water; but at about 160° C. it becomes reddish-brown, and so viscous that it will not run out of an inverted test-tube. At intermediate temperatures it consists of a mixture of these two forms in solution in each other. On further heating, the viscous sulfur grows thin again, and finally boils at about 444° C.—a temperature somewhat above the melting points of lead and zinc.

The vapor of sulfur, at its boiling point, has a density corresponding to the formula S_8 (§ 162). But this decreases very rapidly with increasing temperature, until at a bright red heat practically all the complex molecules are dissociated into simpler ones of the formula S_2.

The different *physical modifications* of an element such as sulfur are known as its *allotropic forms*. These differ widely in their physical properties—color, density, solubility, and the like. Nevertheless, all the modifications of sulfur unite with oxygen to give the same oxides, SO_2 and SO_3. All unite directly with **metals,** when heated, to form metallic sulfides: FeS, ZnS, CuS, etc. All unite with **carbon, chlorine,** and **phosphorus,** to form CS_2, S_2Cl_2, P_4S_3.

227. Uses of Elementary Sulfur.—Elementary sulfur finds a great many important uses. Vast quantities are burned in preparation of **sulfur dioxide** for the manufacture of sulfuric acid (§ 239). It is combined with coke at high temperatures, to produce carbon disulfide (§ 337). The match industry uses considerable quantities of sulfur, in combination with phosphorus (§ 311).

In agriculture sulfur is of rapidly increasing importance. Alone, or mixed with lime, it has long been used to destroy fungi in vineyards and orchards. Sometimes it is mixed with ground phosphate rock and spread on the soil as a **fertilizer** or compost.

In the soil it slowly oxidizes, under the action of bacteria, and the resulting sulfuric acid appears to render the phosphate rock more easily dissolved and absorbed by the roots of plants than would otherwise be the case (§ 314). In some instances a soil may perhaps receive an indirect benefit from sulfur, due to its effect in restraining certain types of microorganisms in the soil, or encouraging the growth of others.

Sulfur has fair mechanical strength, is a very excellent insulator for heat and electricity, and is insoluble in dilute acids. This last quality makes it of use in preparing **acid-proof cements.**

Sulfur is melted, and something more than its own weight of hot sand stirred in. The mixture is poured like concrete, sets very hard, and is about as resistant to corrosion as the sand itself.

A very remarkable property of sulfur is its ability **to toughen and harden rubber** (vulcanizing, § 353).

228. Preparation of Hydrogen Sulfide. A Test for its Presence.—Hydrogen sulfide (formerly called sulfuretted hydrogen) is a colorless, **poisonous** gas, of offensive odor. It occurs in nature whenever plant or animal matter decays in a limited supply of air. **It is prepared in the laboratory by action of dilute hydrochloric acid** (contained in a modified Kipp apparatus, § 71) **on lumps of ferrous sulfide:**

$$2HCl + FeS = H_2S \uparrow + FeCl_2.$$

Any other dilute *non-oxidizing* acid of reasonable activity might be used instead of sulfuric acid; and many other sulfides, such as Sb_2S_3 (but not pyrite, FeS_2).

Is the above reaction complete or incomplete? Why? Which reagent is commonly present in excess during the entire course of the reaction, and why? What two principal dissolved substances are contained in the liquor discarded from the Kipp generator, after the reaction is complete?

Traces of hydrogen sulfide may be detected by bubbling the air or other gas to be tested through a solution of lead acetate. A brownish-black color is developed (**lead sulfide**):

$$H_2S + Pb(C_2H_3O_2)_2 = PbS \downarrow + 2HC_2H_3O_2.$$

A solution of a cadmium salt would be turned yellow (cadmium sulfide). An additional test for the presence of hydrogen sulfide in another gas is of course afforded by its **odor**.

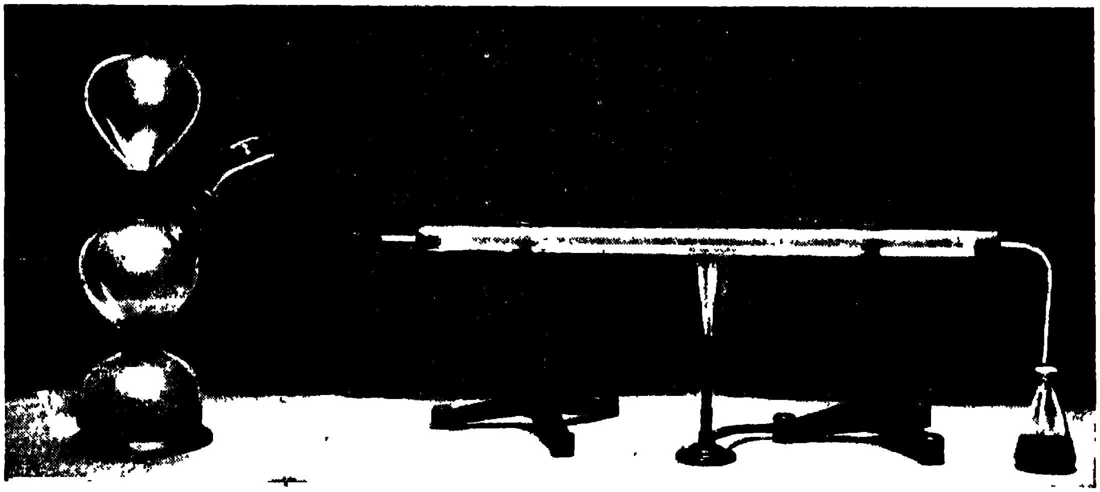

FIG. 63 —Direct union of hydrogen and sulfur.

229. Direct Union of Hydrogen and Sulfur. A reversible reaction.—When hydrogen is passed over sulfur in a glass tube heated to about 300° C. (*A*, Fig. 63) the two elements combine in very insignificant amounts to form hydrogen sulfide, as is indicated by the development of a brownish-black stain in a lead acetate solution contained in a test-glass at *C*. But the reaction is too slow and incomplete to be of any use. The gas that issues from the apparatus is still largely hydrogen in spite of our best efforts, no matter what temperature is used. In fact, the higher the temperature we employ, the worse are the results we get, **for**

the change is reversible, and the reverse reaction is the one that is favored most by the application of more heat:

$$H_2+S \underset{\text{High temperature}}{\overset{\text{Low temperature}}{\rightleftarrows}} H_2S+2730 \text{ cals.}$$

Show that this statement is in harmony with the principle of Van't Hoff (§ 219).

The reverse reaction can be shown very nicely by lighting a jet of hydrogen sulfide and permitting it to impinge against the lower surface of a porcelain dish filled with water. The heat of the burning jet decomposes a part of the gas, and accordingly deposits a film of unburned sulfur against the porcelain. The same effect may be observed if a cylinder of the gas is lighted with a match.

These experiments reveal a dilemma that is often met in trying to carry out a chemical reaction in a useful way. **If we employ too low a temperature a reaction may proceed too slowly to be of any use. Too *high* a temperature may favor the reverse reaction.** We are compelled to steer a pretty narrow course between insufferable slowness and incompleteness. **The only possible way out of such a difficulty is to find a catalytic agent to speed up the desired reaction, and thus make it possible to use a lower temperature than would otherwise be permissible.**

Which of the following reactions (§ 219) can be made more complete *from left to right* by an increase of temperature than would otherwise be permissible; and which need to be carried out at as low a temperature as possible, in the presence of a catalytic agent?

$$CaCO_3 \rightleftarrows CaO+CO_2-43{,}000 \text{ cals.};$$

$$N_2+3H_2 \rightleftarrows 2NH_3+24{,}000 \text{ cals.};$$

$$NH_3+2O_2 \rightleftarrows HNO_3+H_2O+80{,}700 \text{ cals.};$$

$$C+CO_2 \rightleftarrows 2CO-39{,}000 \text{ cals.};$$

$$2SO_2+O_2 \rightleftarrows 2SO_3+45{,}200 \text{ cals.}$$

A minus sign means that heat is absorbed in the left to right reaction.

230. Hydrogen Sulfide as an Inactive Acid. – Review §§ 103, 114. Hydrogen sulfide is one of our most important chemical reagents, in spite of its unpleasant odor, and the danger attending the use of such a poisonous substance.

It dissolves slightly in water, forming a solution having the properties of an extremely inactive acid. Thus by direct union with bases it forms salts and water.

If H_2S is passed into an alkaline solution until it is *saturated* the acid sulfide is formed:

$$NaOH + H_2S = NaHS + H_2O.$$

Half enough H_2S to saturate the solution gives the normal salt:

$$2NaOH + H_2S = Na_2S + H_2O.$$

Sodium acid sulfide, NaHS, less properly called *sodium hydrosulfide*, reacts *neutral* toward litmus; and the normal salt Na_2S is strongly alkaline—facts that prove hydrogen sulfide to be a very inactive acid (§ 114).

231. Hydrogen Sulfide as a Reducing Agent.- **Hydrogen sulfide *reduces* a great many other substances, and is itself oxidized, usually to *water* and *sulfur*.** But a very vigorous oxidizing agent, such as nitric acid, may give sulfuric acid. In either case it is really the sulfur within the hydrogen sulfide that is oxidized, increasing in valence from −2 to 0, or even +6 (compare § 133).

1. A solution of hydrogen sulfide is slowly oxidized by air, becoming milky from separated sulfur:

$$2H_2S + O_2 = 2H_2O + 2S.$$

2. Sulfur dioxide is reduced to sulfur:

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

3. Concentrated sulfuric acid is reduced to water and sulfur:

$$3H_2S + H_2SO_4 = 4H_2O + 4S.$$

4, 5. Potassium permanganate and potassium dichromate, in presence of dilute acids, are reduced to corresponding salts of potassium, manganese, and chromium:

$$KMnO_4 + H_2S + HCl \rightarrow KCl + MnCl_2 + H_2O + S.$$

Balance this by the method of § 135.

Write and balance, similarly, equations for the reduction of potassium permanganate and potassium dichromate by hydrogen sulfide in the presence of sulfuric acid and acetic acid, respectively. Keep proper valences (§ 122).

6. Hot, fairly concentrated nitric acid oxidizes hydrogen sulfide to sulfuric acid, and is itself reduced to nitrogen peroxide, NO_2.

Write and balance equation.

7. Ferric salts, *in acid solution*, are reduced to ferrous salts:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

If the solution is alkaline, ferric salts give a black precipitate of ferric sulfide, Fe_2S_3; and ferrous salts one of ferrous sulfide, FeS.

8. Iodine is reduced by hydrogen sulfide to hydriodic acid (§ 199):

$$I_2+H_2S=2HI+S.$$

Why are we justified in calling this reduction? Describe the process as a transfer of electrons.

232. Hydrogen Sulfide as a Precipitant.—The most important use of hydrogen sulfide is in the chemical laboratory as a **precipitant** (or precipitating agent). Many metals are precipitated as insoluble sulfides by passing a current of hydrogen sulfide gas through solutions of their salts. The metal concerned may often be identified by the color of the precipitated sulfide.

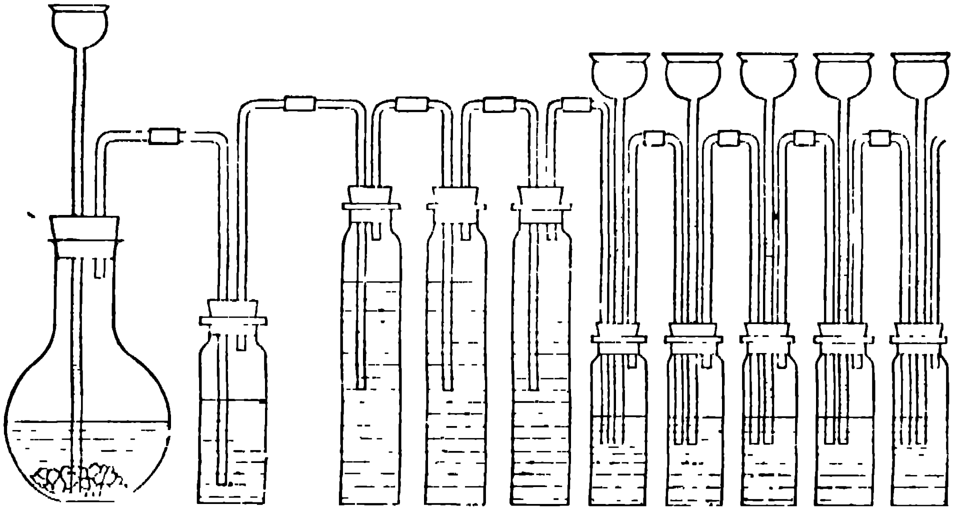

FIG. 64.—Lecture experiment to illustrate the precipitation of the metals as insoluble sulfides, by a current of hydrogen sulfide

In Fig. 64, hydrogen sulfide produced in the generator at the left is passed through a bottle containing a little water, to remove impurities, carried over mechanically in the spray from the generator. The eight bottles at the right contain solutions of the chlorides or acetates of Cu, Cd, Sb, Zn, Mn, Fe, Ni, Ca; in each case in the presence of a small quantity of HCl. The first three of these immediately produce colored sulfides—black, yellow, orange. The sulfides of the metals at the right are not precipitated in the presence of acid. But on adding ammonium hydroxide through the thistle tubes, to neutralize the acid, four more precipitates come down—white, yellowish-pink, black, and black. The calcium is not precipitated, even in an alkaline solution.

This experiment shows that **the metals may be divided into three groups, according to whether they may be precipitated as**

sulfides (1) in the presence of an acid; or (2) only in a neutral or alkaline solution; or (3) not at all. Details had best be postponed until qualitative analysis is begun.

Write equations for the precipitation of solutions of cadmium sulfate, bismuth acetate, lead perchlorate, stannous chloride, and arsenious acid by hydrogen sulfide, forming in each case a sulfide in which the metal has the same valence as it had in the original solution. Balance these five equations.

233. Origin of the Deposits of Native Sulfur.—The reactions of hydrogen sulfide seem to furnish a clue to the way in which the enormous deposits of sulfur were built up in nature. The vapors issuing from volcanoes contain considerable quantities of hydrogen sulfide and sulfur dioxide, formed by the action of acids or water on sulfide and sulfate minerals, at high temperatures. The sulfur dioxide is reduced by the hydrogen sulfide (or by CO, or CH_4), producing deposits of sulfur which often fill all the rock crevices and minor vents (*fumaroles*) around the main volcanic crater.

So-called sulfur springs contain large quantities of dissolved hydrogen sulfide, from contact with sulfide minerals, or from decay of organic matter out of reach of air. When such hydrogen sulfide solutions approach the surface the gas is oxidized by the oxygen of the air, and sulfur deposited. Many minor deposits of sulfur have been definitely traced to this origin.

An interesting side-light on the subject is afforded by the observation that certain microorganisms have the ability to make use of hydrogen sulfide as a source of energy; absorbing this gas, so poisonous for higher forms of life, and oxidizing it into sulfur and water—in much the same way that we ourselves obtain energy for our vital activities by the oxidation within our bodies of fats, sugars, and starches to water and carbon dioxide. It is presumed that the enormous deposits of the southern United States owe their origin in part to this process.

EXERCISES

1. Explain how it is determined that sulfur has the formula S_8 at temperatures just above its boiling point.

2. How many cubic centimeters of hydrogen sulfide gas are required to completely reduce 22.4 cc. of sulfur dioxide? How many milligrams of sulfur are formed?

3. All possible gradations exist between ordinary vulcanized rubber and hard rubber. Is this an argument for or against the assumption of chemical union between the sulfur and rubber, and in what way?

4. How is S_2Cl_2 prepared, and for what is it used?

5. State the circumstances under which catalytic agents are employed, and those under which they are commonly not needed.

6, 7. Review questions in §§ 229, 231.

8. Tell something of the part bacteria play in the transformations of sulfur in nature.

9. What percentage of water is contained in gypsum? What percentage of sulfur in galena?

10. A sample of impure pyrites contains 40 per cent of sulfur. To what percentage of FeS_2 does this correspond?

11. How many liters of hydrogen sulfide gas at standard conditions could be liberated by the action of an acid on 87.9 g. of pure ferrous sulfide?

12. How many cubic feet of sulfur dioxide at standard conditions (§ 174) can be prepared by roasting a ton of impure sulfide ore containing 40 per cent of sulfur.

13. Sulfur is burned, using 50 per cent more air than is needed. Find the percentage by volume of O_2, N_2, and SO_2 in the gases coming from the furnace.

14. A ten-gram sample of an alloy is dissolved in acid, and the antimony contained in the solution precipitated with H_2S. The precipitate, Sb_2S_3, after being separated and dried, weighed 0.3366 g. Calculate the percentage of antimony in the alloy.

15. How many cubic centimeters of hydrogen sulfide gas are needed to precipitate the copper in 50 cc. of a $N/10$ solution of a copper salt? How many milligrams will the precipitate weigh?

16. What is meant by each of the following: catalyser, retarder, concentration, thermochemical equation, chemical equilibrium?

CHAPTER XVIII

THE OXIDES OF SULFUR AND SULFURIC ACID

234. Preparation of Sulfur Dioxide.—Sulfur dioxide is a colorless gas, with the odor of burning sulfur. It is produced:

(1) Commercially, **by burning sulfur or pyrites** (§ 224).

Write and balance equations, assuming the iron in the pyrites to be oxidized to ferric oxide.

(2) In the laboratory, **by reducing concentrated sulfuric acid.**

When concentrated sulfuric acid is heated with metallic copper it is reduced to sulfur dioxide, while the copper is oxidized to copper oxide. We may consider that sulfurous acid, H_2SO_3, is first formed:

$$H_2SO_4+Cu=CuO+\underset{\substack{\downarrow\\ SO_2+H_2O.}}{H_2SO_3}$$

Some of the copper oxide formed always reacts with a part of the excess of sulfuric acid, forming copper sulfate

Write and balance similar equations for the reduction of concentrated sulfuric acid by sulfur, metallic aluminum, and carbon (forming carbon dioxide).

(3) In the laboratory, **by decomposing a sulfite or acid sulfite with a dilute, non-oxidizing acid:**

$$Na_2SO_3+2H_2SO_4=2NaHSO_4+\underset{\substack{\downarrow\\ H_2O+SO_2}}{H_2SO_3}$$

$$NaHSO_3+HCl=NaCl+\underset{\substack{\downarrow\\ H_2O+SO_2}}{H_2SO_3.}$$

Write and balance equation for the decomposition of calcium sulfite by acetic acid. For the decomposition of potassium acid sulfite by phosphoric acid, forming KH_2PO_4. Keep correct valences for elements concerned.

235. Physical Properties of Sulfur Dioxide.—Sulfur dioxide is fairly soluble (about 50 volumes of gas in 1 of water, at room temperature). Like chlorine and carbon dioxide, **it can be condensed**

to a liquid at room temperature by pressure alone, and is sold in liquid form in steel cylinders. Even at atmospheric pressure it is easily liquefied by being passed through a tube packed in salt and ice.

From the formula of the gas determine (§ 154) whether it is heavier or lighter than the air, and in about what ratio.

236. Chemical Properties of Sulfur Dioxide.—1. Sulfur dioxide is **an important bleaching agent.** This property depends on its ability to unite with a good many colored substances to form unstable colorless "addition compounds." (Contrast this with the bleaching action of chlorine.)

Sulfur dioxide is preferred for bleaching silk, feathers, and wool—*nitrogenous material*—for these would be injured by the alkali in bleaching powder. Cotton and linen, on the other hand, which are commonly bleached with bleaching powder, would be weakened by sulfuric acid developed by oxidation on drying them in air, after bleaching with sulfur dioxide.

The juice of the sugar beet is bleached with sulfur dioxide in the manufacture of sugar (§ 367).

2. **A solution of sulfur dioxide in water turns blue litmus red, and is assumed to contain a slightly active acid, sulfurous acid, H_2SO_3.** The acid itself has never been obtained separate from the water in which it is dissolved, its formula being merely inferred from that of its salts: the acid and normal sulfites. It is accordingly referred to as a "hypothetical acid."

If enough SO_2 is passed into an alkaline solution to saturate it (i.e., acid in excess) an **acid sulfite or bisulfite** is formed:

$$NaOH + SO_2 = NaHSO_3.$$

The **normal sulfite** is prepared by dividing a solution of sodium hydroxide into two equal parts, saturating one with SO_2, and then adding the other. (Write equations.)

How would you prepare a solution of calcium bisulfite, $Ca(HSO_3)_2$? Write equation. This reaction is of great importance in paper-making (§ 371).

From the character of sulfurous acid (slightly active) predict the action (§ 114) toward litmus of a solution of sodium sulfite.

3. **Sulfur dioxide is a good reducing agent. When it reduces another substance it is itself oxidized to sulfuric acid.**

a, b Potassium permanganate and potassium dichromate, in presence of dilute sulfuric acid are reduced to sulfates of K, Mn, Cr (Valences, § 122).

c. Nitric acid is reduced to nitric oxide, NO.
d. Iodine (in presence of water) is reduced to hydriodic acid.
Write equations for these four reactions, and balance according to § 135.

Note that sulfur dioxide and hydrogen sulfide are alike in having **acid properties** and **reducing properties** when dissolved in water.

But sulfur dioxide cannot be used as a precipitant after the fashion of hydrogen sulfide—for sulfites of the heavy metals, although very slightly soluble in water, are measurably more so than the corresponding sulfides; and enter into the reverse reaction:

$$FeSO_4 + H_2SO_3 \rightleftarrows H_2SO_4 + FeSO_3.$$

Equilibrium is reached before enough heavy-metal sulfite is formed to saturate the solution and permit a precipitate to appear.

237. Thiosulfates.—Closely related to the sulfites are the *thiosulfates*. Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, is commonly called "hypo." A solution of this salt is **an excellent solvent for silver salts insoluble in water,** and is used for this purpose in photography, as a fixing bath (§ 545). In the bleaching industry it is used to combine with and remove any trace of chlorine that may remain in the cloth after the bleaching process (§ 185).

Sodium thiosulfate is commonly *prepared* by dissolving powdered sulfur in a hot solution of sodium sulfite:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

A solution of sodium thiosulfate is an important reagent in the chemical laboratory. It decolorizes iodine solutions:

$$2Na_2S_2O_3 + I_2 = \underset{\substack{\text{Sodium} \\ \text{tetrathionate}}}{Na_2S_4O_6} + 2NaI;$$

and is used as a means for determining how much iodine is present in solutions of unknown concentration (*iodimetry*).

In spite of the trade name, "hypo," and the occasional designation sodium hyposulfite, sodium thiosulfate is different from the true sodium hyposulfite, $Na_2S_2O_4$. This is formed by the reduction of a solution of sodium bisulfite with zinc, and is of commercial importance as a reducing agent in dyeing cloth with indigo dye.

238. Sulfur Trioxide, SO_3.—Whenever sulfur burns in the air a small quantity of SO_3 is formed in addition to the main product, SO_2. Sulfur trioxide **is most conveniently formed by passing sulfur dioxide mixed with an excess of air or oxygen, through a**

moderately heated tube containing ferric oxide or platinum-coated asbestos to serve as a catalytic agent:

$$2SO_2+O_2 \rightleftarrows 2SO_3+45{,}200 \text{ cals.}$$

We meet the same difficulty here that was observed in the attempt to prepare hydrogen sulfide by direct union of hydrogen and sulfur (§ 229). Too low a temperature means too slow a reaction rate; too high a temperature favors the reverse reaction (§ 219). We accordingly compromise on about 400° C. With a catalyzer the reaction is fast enough at this temperature, using a large excess of oxygen, to convert about 98 per cent of the SO_2 into SO_3 during passage through the tube. Why an excess of oxygen (§ 217)?

Sulfur trioxide, or **sulfuric anhydride,*** is a colorless liquid, quickly transformed into a snow-white solid (S_2O_6) with much the appearance of asbestos, on standing in contact with a trace of moisture. Both substances unite vigorously with water to form sulfuric acid.

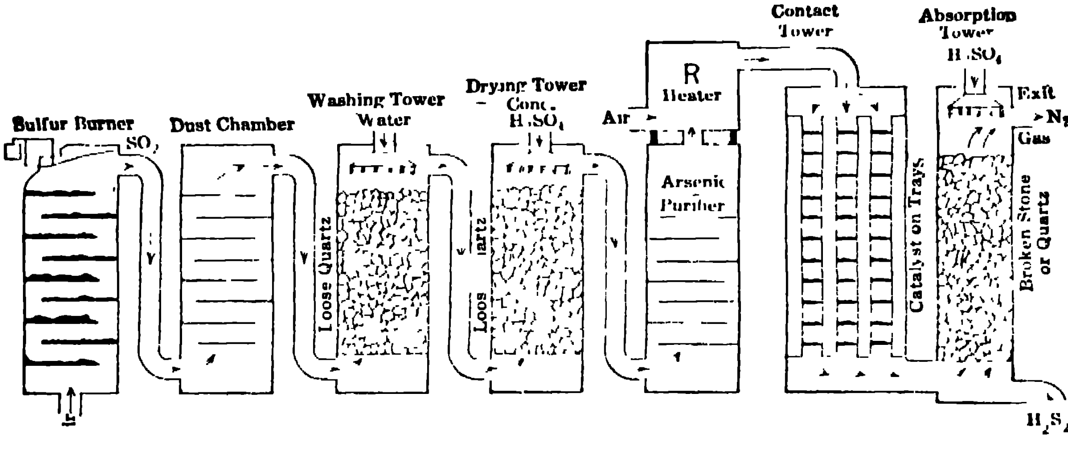

FIG. 65 —Manufacture of sulfuric acid by the contact process

239. Contact Process for Manufacturing Sulfuric Acid.—The process just outlined is the basis of the **contact or catalytic** process for the manufacture of sulfuric acid.

Sulfur or pyrites is burned in the air to SO_2. This gas is cooled and freed from dust; washed with water, then dried by being passed upward through a tower filled with quartz or coke, down which trickles concentrated sulfuric acid. Arsenic compounds are next removed by passing the gas over a series of shelves filled with ferric oxide. The purified gas is then mixed with air, heated in a regenerator (*R*, Fig. 65), and passed into a contact tower, containing a catalytic agent (Fe_2O_3). Here sulfur dioxide unites with oxygen to form sulfur trioxide, and releases a considerable quantity of heat, which is used in warming fresh quantities of incoming gases in the regenerator:

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* An *acid anhydride* is a non-metallic oxide, capable of forming an acid by direct union with water (§ 101).

$$2SO_2+O_2=2SO_3+45{,}200 \text{ cals.}$$

It happens that the sulfur trioxide vapors thus produced tend to form a mist of fine droplets, which can be bubbled right through water without being dissolved. But they are absorbed quite readily by bringing them into contact with a spray of concentrated sulfuric acid. Thus we form "fuming sulfuric acid," $H_2S_2O_7$, which yields ordinary concentrated sulfuric acid on being diluted with a quantity of water equivalent to the SO_3 which it has dissolved.

$$H_2S_2O_7+H_2O=2H_2SO_4.$$

240. The Chamber Process.—A great deal of dilute sulfuric acid is still manufactured by the **chamber process.** This is carried out in three operations:

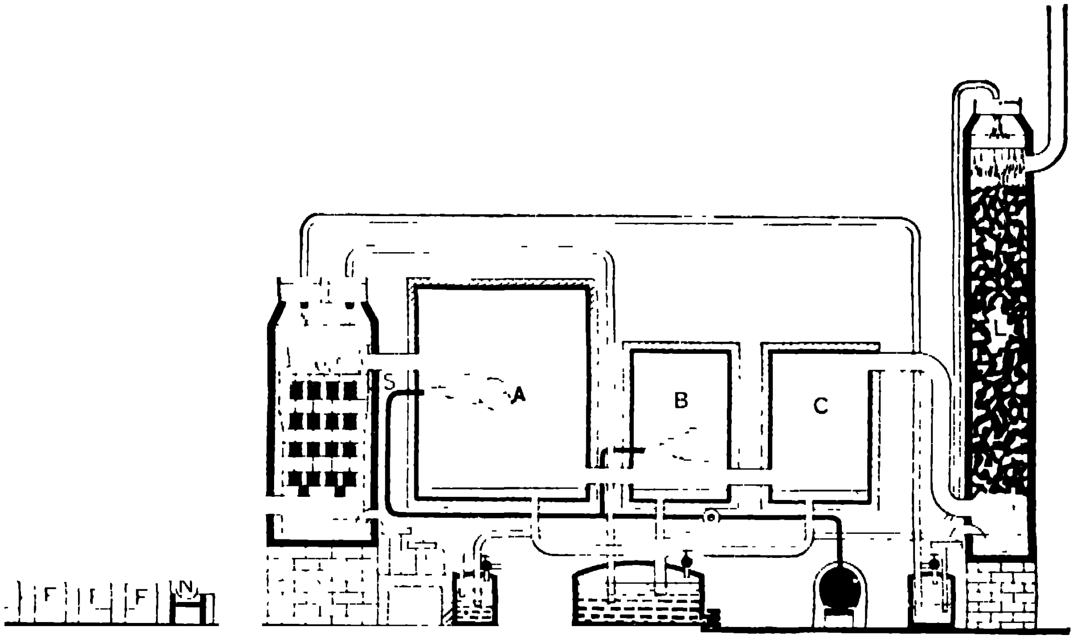


FIG. 66—Manufacture of sulfuric acid by the chamber process.

1. Pyrite or sulfur is burned to SO_2 in a large excess of air, in a row of small furnaces or pyrite burners (*F*, *F*, Fig. 66).
2. The SO_2 is mingled with steam and nitric acid fumes; and in the presence of atmospheric oxygen is oxidized to dilute sulfuric acid, as it slowly drifts through a series of three to six lead-lined reaction chambers (*A*, *B*, *C*), each the size of a small lecture hall (100×40×40 ft.).

The reactions involved in this process of oxidation, stripped of all unnecessary details, amount to this:

(*a*) The nitric acid fumes, introduced in part at *N* and in part in the tower

G, consist of NO_2, O_2 and water vapor; but, ignoring the excess of oxygen, may for simplicity be represented by the formula of nitric acid itself, written $OH \cdot NO_2$. By direct addition to SO_2 we then get $SO_2(OH)(NO_2)$, which is *nitrosyl sulfuric acid*, a substance forming beautiful white crystals, resembling frost patterns.

(*b*) This nitrosyl sulfuric acid is immediately decomposed by the excess of steam (double decomposition), forming dilute sulfuric acid:

$$SO_2(OH)(NO_2) + HOH = \underset{\text{Sulfuric acid}}{SO_2(OH)_2} + \underset{\text{Nitrous acid}}{HNO_2}.$$

(*c*) The nitrous acid fumes thus produced are reoxidized to nitric acid by the excess of air in the succeeding chambers, and used over again. The oxygen of air, and not nitric acid, is, in the last analysis, the real oxidizing agent in the chamber process. The nitric acid fumes merely aid in the *transfer* of the oxygen and thus, in a sense, play the part of a catalyzer. This reoxidation of nitrous fumes by the air takes time, consequently the chambers must be numerous enough and large enough to keep the mixed gases from drifting through too rapidly.

(*d*) But these nitrous fumes cost money. When leaving the last chamber they must not be permitted to escape, but are dissolved in a spray of concentrated sulfuric acid (in the Gay-Lussac tower, *L*) elevated with compressed air, and reintroduced into the system (in the Glover tower, *G*). The two towers, then, are simply a scheme for saving nitrous acid fumes. One dissolves these, the other puts them back into the system—a beautiful example of a reversible reaction:

$$\underset{\substack{\text{Concentrated}\\\text{sulfuric acid}}}{SO_2(OH)_2} + HNO_2 \underset{\text{Glover tower}}{\overset{\text{Gay-Lussac tower}}{\rightleftarrows}} \underset{\substack{\text{Nitrosyl}\\\text{sulfuric acid}}}{SO_2(OH)(NO_2)} + HOH.$$

The water used in reversing this reaction, in the Glover tower, is usually introduced in the form of dilute sulfuric acid, drawn from the bottom of one of the chambers, as shown in the sketch. If the two towers operated perfectly the process would run indefinitely, after once being started, without introducing more nitric acid. But in practice there is some loss of nitrous fumes, and a few pounds of nitric acid need to be prepared (§ 297) and introduced from the niter-pot, N, for every ton of sulfuric acid manufactured.

Before leaving the subject of the manufacture of sulfuric acid the student should note that the contact and chamber processes both operate on the same principle: **The oxidation of SO_2 by the oxygen of the air, adding enough water to form H_2SO_4.** But the steps by which this result are obtained are different in the two processes; and in the chamber process we are able to identify an **intermediate product,** $SO_2(OH)(NO_2)$, which explains how the catalyzer does its work.

The contact process may produce sulfuric acid of any concentration. The chamber process, on the other hand, gives only dilute sulfuric acid, since concentrated acid would attack the lead linings of the chambers. Chamber acid may be concentrated by evaporation, preferably by being heated while trickling down a cascade system constructed of trays of fused silica (§ 400); but much of it is used directly in the diluted condition, for the manufacture of superphosphate fertilizer (§ 314).

241. Properties of Sulfuric Acid.—Sulfuric acid is a heavy, oily liquid, miscible with water in all proportions, and quite colorless if pure. It freezes into beautiful crystals at a few degrees below zero. It is easily decomposed, at temperatures near its boiling point, into H_2O and SO_3; and the latter in turn, to a slight extent, into SO_2 and O_2. When the concentrated acid is poured into water, a great deal of heat is liberated—evidence that, in this case, the act of solution is not a simple mixing of the two substances, but **a chemical combination between the acid and the water.**

The chemical behavior of sulfuric acid varies with its concentration. In *dilute solution* it is an **acid** of moderate activity. In *concentrated solution* it is an **oxidizing agent** and a **dehydrating agent.**

1. **Acid Properties** (shown in dilute solution). Compare (§ 179).

(*a*) Many metals (most conspicuously those above hydrogen in the electrochemical series) dissolve in dilute sulfuric acid to form sulfates, the action being the more vigorous the higher the position of the element in the series.

Write equations for the solution in dilute sulfuric acid of such of the following metals as dissolve in it appreciably, at room temperature: Na, Sn, Cu, Fe, Al. (When Sn or Fe dissolves in an acid in the absence of air it forms the salt of lower valence).

(*b*) Displaces H_2S, SO_2, and CO_2 from sulfides, sulfites, carbonates.

Give equations to illustrate.

(*c*) Reacts directly with metallic oxides and bases to form sulfates (acid or normal) and water.

Write and balance equations for the preparation in this way of the normal sulfates of ammonium, calcium, ferric iron.

Under what conditions do sulfuric acid and sodium hydroxide unite to form the acid sulfate, and under what to form the normal sulfate?

2. **Oxidizing properties** (shown in concentrated solution). Concentrated sulfuric acid contains about 95 per cent H_2SO_4 and

5 per cent water. If cold, it acts on iron and most other metals more slowly than when dilute, apparently because the sulfate formed is but slowly soluble in the concentrated acid, tends to coat the surface of the metal over, and thus retards the action. **But when concentrated sulfuric acid is heated, its oxidizing properties come into play, and almost any metal or non-metal, regardless of its position in the electrochemical series, is oxidized and dissolved.**

Recall the action of hot concentrated sulfuric acid on copper (§ 234–2).

Recall the action of concentrated sulfuric acid on hydriodic acid (§ 192). Write equation.

3. **Dehydrating properties** (shown in concentrated solution).

Concentrated sulfuric acid has a strong tendency to unite with water, and is commonly used in the laboratory to dry gases. It is such a powerful dehydrating agent that it decomposes substances like sugar and paper, which contain water in chemical combination. The residue, in the case of sugar, is a porous black mass, mainly carbon. But there is always an odor of sulfur dioxide, evidence that the sulfuric acid has oxidized the material to a slight extent, and been itself reduced.

242. Test for Sulfates.—Only the univalent metals form acid sulfates ($NaHSO_4$, $KHSO_4$). These are strongly acid toward litmus.

Acid sulfates and sulfates, as well as sulfuric acid itself, give a precipitate of barium sulfate when treated with a soluble barium salt:

$$NaHSO_4 + BaCl_2 = BaSO_4 \downarrow + NaCl + HCl.$$

The precipitate formed should prove insoluble in HCl. If it dissolves it may be barium phosphate, carbonate, etc. **The formation of a white crystalline precipitate, insoluble in dilute acids, on adding barium chloride to an unknown solution, is a test for a sulfate.**

243. Uses of Sulfuric Acid and Other Compounds of Sulfur.—We meet compounds of sulfur, particularly sulfuric acid and its salts, in almost everything we do. The water of our domestic supply is often clarified with aluminum sulfate (§ 82) or freed from algae with copper sulfate. Our soap is sometimes made from fat, with the aid of a catalytic agent prepared from sulfuric acid; or else with the aid of caustic soda, a substance often made by a process calling for sulfuric acid (§ 135). The bristles of brushes are often softened with dilute sulfuric acid.

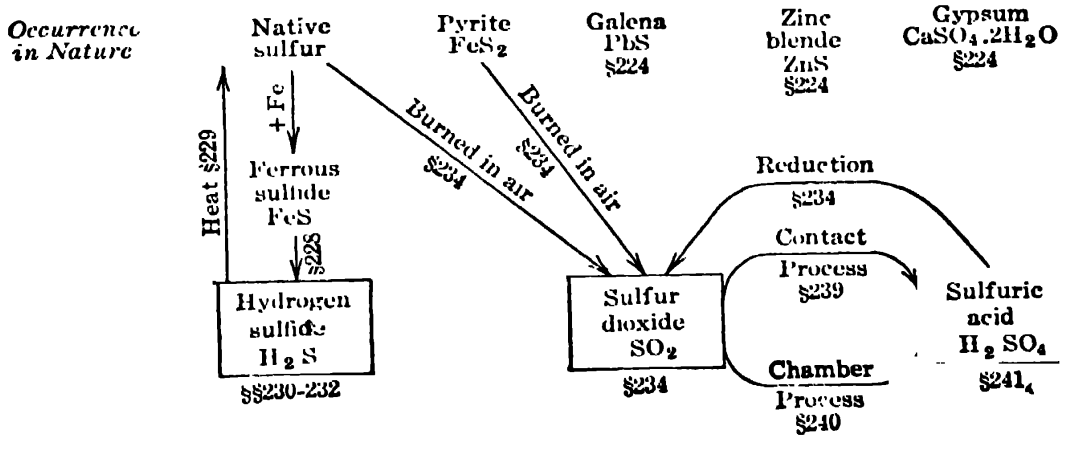
The wool of our clothing is scoured with sulfuric acid, and bleached with sulfur dioxide, and the dyestuffs are fixed in the fiber with aluminum sulfate. The dyes themselves require sulfuric acid at several stages of their manufacture. The leather of our shoes is often prepared and tanned with the aid of arsenic sulfide and chromium sulfate. Shoe-blacking contains animal charcoal, purified with dilute sulfuric acid.

At the table we meet glassware prepared from sodium sulfate (§ 406). We may be served with cereal grown upon land fertilized with ammonium sulfate, gypsum (calcium sulfate), or superphosphate (made by the action of dilute sulfuric acid on phosphate rock, § 311). The very chinaware may carry a pattern of ultramarine blue, a sulfur compound Sugar is often whitened by sulfur dioxide (§ 367); and corn syrup is made by treating starch (§ 369) with dilute sulfuric acid, or an acid (HCl) derived from it. Our newspapers contain wood pulp, which requires calcium bisulfite in its preparation (§ 371), and often contain a trace of ultramarine. Printers' ink often calls for sulfuric acid in its manufacture.

If we own an automobile we meet sulfuric acid in the storage battery, and various compounds of sulfur in the tires. Certain parts of the car were prepared for enameling by pickling in dilute sulfuric acid. The nickel-plated fixtures were all plated in a bath containing nickel ammonium sulfate. Whether the upholstering is of real or artificial leather, sulfur compounds went into its preparation. The top is of fabric, impregnated with cellulose esters, prepared with the aid of sulfuric acid. Cellulose esters appear again in the celluloid windows and the body lacquer. The gasoline we burn comes from petroleum, purified by sulfuric acid (§ 343). Our roadways are cut through rocky outcrops by blasting with dynamite, a substance requiring sulfuric acid in its manufacture (§ 370). Even the Portland cement used in constructing concrete bridges, culverts, or roadbed always contains a small amount of calcium sulfate (§ 465).

We meet other sulfur compounds in our fountain pen, typewriter, telephone, varnish on our office furniture, writing paper, and the lithographed calendar on the wall. Even in our moments of relaxation we fail to escape from the compounds of sulfur, for cinematograph films, the insulation of wireless sets, piano keys, and a violin have met sulfuric acid, or substances prepared with the aid of sulfuric acid, at some stage of their manufacture. Indeed, our last act, when we retire at night, may be to turn a sulfur-rubber switch, thus breaking an electric circuit, consisting of copper wire, purified by electrolysis in a bath containing copper sulfate and sulfuric acid.

244. Graphical Summary.



	Hydrogen Sulfide	Sulfur Dioxide	Sulfuric Acid
Acid properties	slightly active acid	+ H_2O – fairly active acid	active acid
Oxidizing or reducing	reducing	reducing	oxidizing (if conc.)

	Hydrogen Sulfide	**Sulfur Dioxide**	**Sulfuric Acid**
Behavior when heated	$\rightleftarrows H_2+S$	unchanged	$\rightleftarrows 2H_2O+2SO$ $2SO_2+O_2$
Other properties	precipitant	bleaching agent	dehydrating agent (if conc.)
Chief uses	separating and identifying metals in qualitative analysis	bleaching, manufac. of paper. manufac. of sulfites and thiosulfates; manufac. of H_2SO_4	prep of superphosphate; cleaning metals; purifying gasoline, § 343; manufac dyes; explosives, other acids, §§ 105, 297.

EXERCISES

1. Review questions in §§ 234-236, 241.

2. From the known properties of the substances concerned write an equation for the reaction that will probably take place when—

(*a*) Hydrogen sulfide saturates a solution of ammonium hydroxide.

(*b*) Iron is heated with sulfur.

(*c*) Silver is boiled with dilute sulfuric acid.

(*d*) Silver is boiled with concentrated sulfuric acid.

(*e*) Calcium bisulfite is treated with acetic acid.

(*f*) Hydrogen peroxide is added to a solution of hydrogen sulfide.

(*g*) Sulfur is oxidized by concentrated nitric acid.

3. How could you demonstrate that sulfur dioxide has the formula SO_2, rather than S_2O_4?

4. What weight of sulfur needs to be burned to form a liter of concentrated sulfuric acid, sp.g. 1.84 (§ 146), 98 per cent pure?

5. Write equations for the several steps necessary in the preparation of sodium thiosulfate, starting from sodium hydroxide and sulfur.

6. What weight of lead sulfate can be prepared from 100 cc. of N/10 sulfuric acid solution?

7. Starting with sulfur, how would you prepare, in succession: sulfur dioxide, calcium bisulfite, sulfur dioxide, sulfur. Write equations.

8. Explain why a copper sulfate solution is never neutral toward litmus.

9. How many milligrams of sulfur are contained in 10 cc. of N sodium sulfate solution?

10. What volume of sulfur dioxide gas is needed to prepare 1 liter of N/10 sulfurous acid solution?

11. What volume of sulfur dioxide gas can be prepared from the sulfur in 1000 kg. of an ore containing 15 per cent zinc sulfide?

12. From the atomic weight of sulfur estimate its approximate specific heat. State the principle involved.

13. Use your knowledge of sulfur to predict that of selenium in the following respects:

(*a*) Oxide formed when selenium burns in air.

(*b*) Nature of the compound formed when this oxide dissolves in water.

(*c*) What happens when elementary selenium is heated with metals.

(*d*) Formula and chief chemical properties of selenium hydride.

14. At what temperature will 6.4 kg. of sulfur dioxide gas occupy a volume of 250 liters, under a pressure of 10 atmospheres?

15. What is the molecular weight of a gas, 1 g. of which occupies 112 cc., at 745 mm., and 20° C.

CHAPTER XIX

IONS AND ELECTRONS

Some of the most spectacular of recent achievements in science concern the relation of matter to electricity. These researches have given us X-rays and radio, and promise much more through the glimpse they have afforded of the nature of matter and energy. To know these more intimately is to control them more completely. The present chapter will review and amplify the previous discussion (§§ 101, 103, 107).

245. A Century of Electrical Development.—The story of what led up to these latest marvels of science takes us back to the early days of electrical experimentation, when Galvani, in Italy, was watching the nervous twitchings of frog's legs, when stimulated by electrical discharges (1790), and Franklin, in America, was drawing electricity from a thunder-cloud down a wet kite string (1752). These experiments, and others that followed, showed that electrical phenomena of different kinds are really closely related. Electricity causes definite effects according to definite laws, whether it is produced by rubbing a rod of sealing-wax with silk, by air currents in a thunder-cloud, by chemical action, by heat, by movement of an electrical conductor in a magnetic field, or by the "living-dynamo" of the electric eel.

But with convenient means for producing electric currents by chemical action (§ 421) practical chemical applications were not long delayed. Nicholson and Carlisle, in England (1800) decomposed water by the electric current. Then Sir Humphry Davy produced metallic sodium and potassium (1807) and several other new metals by electrolysis (§ 430); and Michael Faraday (1834) discovered the law that bears his name, and which enables us to predict how much chemical change will take place in an electrolytic cell when a definite amount of electricity is passed through it (§ 428). About the same time Robert Hare (§ 32), in America, invented the electric furnace.

Finally, Moissan, in France (1886) succeeded in producing elementary fluorine by electrolysis (§ 197); while metallic aluminum (1886), electrolytic copper (§ 531), calcium carbide (§ 457) and a dozen other electrochemical products became important commercial commodities. These latest developments appeared in a generation that witnessed the invention of the first practical electric dynamo (1870), the telephone (1876), carbon arc and incandescent lighting (1878) and the electric railway.* The apparently trivial experiments of the preceding century, with frogs' legs, kites, and rods of sealing wax, had laid the foundations of a great science, which has altered the whole aspect of civilization.

246. Some Questions to be Answered.—But the more familiarly electricity was applied in the great new industries the more insistently certain facts concerning it demanded explanation:

Why do certain substances conduct an electric current very well, and others scarcely at all?

Why do substances, like sodium chloride, that are non-conductors when in solid form, become conductors when melted or dissolved?

Why is a copper wire not permanently altered, when a moderate current is passed through it, while water is decomposed?

Why does chemical action in electrolysis occur only at the electrodes?

Why is it sometimes the water and sometimes the dissolved substance that is decomposed when an electric current is passed through a solution?

Why are dissolved substances, when a current passes, always moved through a solution and concentrated around one of the electrodes, even when they are not themselves decomposed?

Why are gases, at ordinary pressures, poor conductors of electricity, becoming good conductors at low pressures, and poor conductors again at very low pressures?

These were, for the most part, unsolved riddles some forty years ago. A general theory was needed, to explain why things happened as they did, and to make electricity itself something less of a mystery.

247. Instantaneous Reactions between Acids, Bases, and Salts.—Now whenever the questions raised in a given field of investigation become too numerous or troublesome, the clue to their solution is very apt to come from workers in a neighboring specialty. Thus in the present instance some questions almost purely electrical received their answer through a study of the matters apparently quite unrelated—the chemical and physical properties of acids, bases, and salts.

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* See the splendid historical introduction to the article "Electricity," in the "Encyclopaedia Britannica."

Acids, bases, and salts are remarkable for the readiness with which they exchange atoms or groups of atoms with each other.

Thus when a solution of a silver salt is added to a solution of hydrochloric acid or any metallic chloride salt an **instantaneous** double decomposition occurs, producing a precipitate of silver chloride. But a solution of a silver salt added to a solution of chloroform ($CHCl_3$) produces no result. Chloroform is not a salt, and its chlorine is not so readily exchanged for other non-metals or non-metallic radicals.

Again, when a solution of acetic acid ($HC_2H_3O_2$) is mixed with a solution of the base, sodium hydroxide ($NaOH$) an instantaneous reaction occurs, forming water. But the reaction between acetic acid and ethyl alcohol (C_2H_5OH) proceeds very deliberately, and at room temperature becomes reasonably complete only after the lapse of several weeks. Ethyl alcohol is not a base, and its hydroxyl is not readily exchanged for other non-metallic elements or radicals.

Of course reactions between acids, bases, and salts are not the only instantaneous ones. If they were we should have less respect for dynamite. But ***instantaneous* reactions in which *dissolved substances* exchange atoms of radicals are practically limited to those in which the reacting substances are acids, bases and salts.** It begins to look as if every molecule of an acid, base, or salt were perhaps so constructed as to permit atoms of hydrogen or metal to part company with the rest of the molecule, at the slightest provocation—as if a molecule of silver nitrate, for example, were easily resolvable into two separate particles, a silver atom and a nitrate radical. But let us look farther before deciding that question.

248. Physical Properties of Aqueous Solution of Acids, Bases, and Salts.—The free and easy way in which acids, bases, and salts exchange atoms or groups of atoms is not their only peculiarity. In a former chapter (§ 158), we found that in many cases equal numbers of gram-molecules of different substances, dissolved in a liter of water, are of equal effect on freezing points, boiling points, vapor pressures, or osmotic pressures. But we also noted that **aqueous solutions of acids, bases, and salts have lower freezing points and vapor pressures, and higher boiling points and osmotic pressures than would be expected from the number of gram-molecules of dissolved substance.**

Thus 1 gram-molecule of glycerol, cane sugar, or ethyl alcohol, dissolved in a liter of water, lowers the freezing point of the latter to −1.86° C. But a gram-molecule of sodium chloride or hydrochloric acid produces nearly twice, and one of calcium chloride between two and three times that lowering.

249. Electrically Charged Particles in a Common Salt Solution. —The abnormally great lowering of the freezing point in a solution of an acid, base, or salt would be explained if we could assume that some of the dissolved molecules are decomposed by the process of dissolving them, each fragment of a molecule producing the same effect on the freezing point as one of the original molecules.

But this idea at once gets us into difficulties. For sodium chloride gives an abnormally great lowering of the freezing point of water, yet if a molecule of sodium chloride were to be broken up, it is hard to see how the resulting fragments could be anything else than atoms of the two elements, sodium and chlorine. On dissolving sodium chloride in water we would then get metallic sodium, which would react with the water to liberate hydrogen; and chlorine gas, which would be betrayed by its odor and greenish color. How different from the known properties of a solution of common salt!

Arrhenius, the Swedish chemist who developed the theory we are discussing, tried to get around these difficulties by assuming that the fragments of molecules formed by dissolving sodium chloride in water are not ordinary atoms of sodium and chlorine at all, but **electrically charged** atoms, the sodium atom assuming a positive, and the chlorine atom a negative charge:

$$NaCl \rightleftarrows Na^+ + Cl^-.$$

The double arrow signifies that we probably have to do with a reaction that is reversible and therefore incomplete, only part of the molecules of sodium chloride being decomposed in the process of dissolving them, while the rest remain unchanged.

The electrical charges are assumed to give the charged atoms, Na^+ and Cl^-, quite different properties from those possessed by ordinary atoms of these elements, even depriving sodium of its property of reacting with water and chlorine of its green color and disagreeable odor.

This may seem a very improbable assumption. But it looks more reasonable when we consider that it is energy which determines the properties of matter. We here have to do with electrical energy, carried in very considerable charges, on the individual atoms.

250. The Ionic Theory.—The existence of electrically charged fragments of molecules in aqueous solutions is supported by quite another set of facts. **Aqueous solutions of acids, bases, and salts conduct the electric current.** What more natural than to assume that this is because the charged particles *travel through the solution*, carrying their charges with them, and thus ferry the electricity across from one electrode to the other. For this reason they have been called **ions** (Greek, *going*). But solutions of such substances as cane sugar or alcohol are non-conductors of the electric current, presumably because they contain no ions, but only uncharged molecules. This is quite in agreement with the observation that such solutions have quite normal freezing points.

To summarize: **Acids, bases, and salts, dissolved in water, readily exchange atoms or groups of atoms. Such solutions, furthermore, have abnormally low freezing points and conduct an electric current.**

We explain these facts by assuming that the molecules of dissolved acids, bases, or salts are in part dissociated (§ 101) **into electrically charged particles called ions. These, presumably, have the same effect on the freezing point as ordinary molecules; but serve also, in electrolysis, to transport electricity through the solution from one electrode to the other.** This is the fundamental idea of the **ionic theory,** as stated by Arrhenius, in 1887.

The three classes of substances which furnish conducting solutions when dissolved in water are called **electrolytes.** Substances which do not, such as cane sugar or alcohol, are called **non-electrolytes.**

251. Electrical Charges on Ions.—But granting the possible existence of ions, or electrically charged fragments of molecules, another question looms up. Do all ions carry the same electrical charge, or do some carry more electricity than others; and are some perhaps positive, and others negative?

We have a clue to this riddle when we recall (§ 167) that hydrogen and the metals, with few exceptions, migrate during electrolysis in the direction of the *negative* electrode (cathode) and are there separated; while the non-metals are separated at the *positive* electrode (anode). But the rule is that unlike charges of electricity attract. It must therefore follow that **ions of hydrogen and the metals carry positive, and ions of the non-metals negative charges.** Examples, H^+, Na^+, Cl^-, NO_3^-.

Since the positively charged ions all move in the direction of the cathode during electrolysis they are frequently called **cations;** while the negatively charged ions are called **anions.**

We think of the electricity passing through a cell during a process of electrolysis as being transported through the solution by the movement of the individual ions. As soon as the circuit is closed the ions within the solution begin to move—cations toward the cathode, and anions toward the anode. An ion which happens to be very close to an electrode arrives there immediately; others may not arrive for hours. But as they come up, one by one, they may (or may not) discharge their electricity into the electrode, and make their appearance as ordinary atoms or molecules—chlorine, hydrogen, metallic copper, and so forth.

Now experiments show that **the quantity of electricity passing through an electrolytic cell while one gram-atom of an element is being dissolved, transformed or separated at an electrode is proportional to the valence of that element**—twice as much for one gram-atom (=65.37 g.) of zinc (Zn^{II}), and three times as much for one gram-atom (=27.1 g.) of aluminum (Al^{III}), as would be needed for a gram-atom (=1.008 g.) of hydrogen. This is **Faraday's Law,** discussed more completely in a later chapter (§ 428).

This proves that **each individual ion carries an electrical charge directly proportional to the valence of the corresponding atom or group.**

Thus if the hydrogen ion is represented by H^+, that of zinc must be Zn^{++}, and that of aluminum Al^{+++}. Giving negative signs to anions, the chlorine ion must be Cl^-, the sulfate ion SO_4^{--}, the phosphate ion PO_4^{---}, and so forth.

252. Polar and Non-polar Solvents.—Water is not the only solvent that furnishes conducting solutions, by causing dissociation of the dissolved substance into ions. Liquid NH_3, liquid SO_2, liquid HCN, and liquid HF (§ 197) are about as effective as water itself. Many organic solvents, such as alcohols and acids,* also dissolve electrolytes to form solutions having noteworthy conductivity.

These substances (and water itself) are all characterized by a comparatively great *chemical activity*. They enter into numerous chemical reactions with each other, even at room temperature. As a group they are often referred to as **polar solvents.**

But the organic hydrocarbons—substances containing hydrogen and carbon only—as well as certain related halogen and sulfur compounds are comparatively inert chemically. These **non-polar solvents are not only nearly perfect insulators themselves, but fail to furnish conducting solutions when other substances are dissolved in them.** Examples are hydrocarbons and hydrocarbon mixtures like benzene, gasoline, and kerosene; and such things as chloroform and carbon bisulfide.

253. Conductivity of Molten Salts and Alkalies.—Many crystalline salts become pretty fair conductors when they are heated to temperatures just below their melting points; and **when actually melted, all salts, and the caustic alkalies** (NaOH, KOH) **conduct well.** Thus heat is able to dissociate certain substances into ions.

This fact is put to practical use on a commercial scale in the preparation of metallic sodium by electrolysis of fused NaCl or NaOH (§§ 432, 433). Many other metals (K, Be, Mg, Ca, Ba) have been prepared in a similar way by the electrolysis of their fused chlorides.

254. Formulation of Electrolytic Dissociation.—The process of decomposing a substance into its ions is called **electrolytic dissociation** in spite of the fact that it has nothing directly to do with electrolysis, but is brought about by the very act of dissolving the given substance in the polar solvent. The only effect of an electric current on such a solution is to cause ions already present to move up to the electrodes and there deliver their electric charges. It is even thought that ions may pre-exist in a crystal of such a substance as sodium chloride, in advance of its solution in water.

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* Also organic aldehydes, ketones, nitriles, and amines.

Electrolytic dissociation is also often called **ionization.** It is presumably always to be formulated as a reversible reaction:

$$Na_2CO_3 \rightleftarrows 2Na^+ + CO_3^{--};$$

$$\begin{array}{l} NaHCO_3 \rightleftarrows Na^+ + HCO_3^-; \\ \qquad\qquad\qquad\qquad\quad \uparrow\downarrow \\ \qquad\qquad\qquad\qquad H^+ + CO_3 \end{array}$$

$$Al_2(SO_4)_3 \rightleftarrows 2Al^{+++} + 3SO_4^{--};$$

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-;$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

In writing ionic equations this text will employ a dotted arrow whenever a reaction is very incomplete. Thus the preceding equations indicate that the three substances first listed are assumed to be very largely dissociated into ions, and that there is but a slight tendency for these to recombine to form molecules. But the last two equations show that acetic acid and ammonium hydroxide are presumed to persist very largely as molecules when dissolved in water, and form but comparatively few ions. The reasons for these assumptions will be given hereafter.

We may also notice that **the groups or radicals of ordinary molecules remain undecomposed in forming ions.** They simply assume charges as a whole. Note also that **all acids furnish H^+ ions, and all bases OH^- ions, when dissolved in polar solvents.**

Which of the following substances are electrolytically dissociated when dissolved in water:

$Ca(OH)_2$, KCN, NH_4NO_3, $(CH_3)_2CO$, $HClO$, C_6H_5OH, $NaNH_4HPO_4$, $C_6H_{12}O_6$.

Formulate the dissociation when it occurs.

255. Acids Dissociate in Stages.—It should be noted that **acids having more than one replaceable hydrogen atom in a molecule**—such as H_2SO_4, H_2CO_3, H_3PO_4 . . . **dissociate in successive stages:**

$$H_2SO_4 \rightleftarrows H^+ + \underset{\text{Hydrosulfate-ion}}{HSO_4^-};$$

$$HSO_4^- \rightleftarrows H^+ + \underset{\text{Sulfate-ion}}{SO_4^{--}}.$$

The second stage is always much less complete than the first, and third (if any) less complete than the second. Thus phosphoric acid behaves in certain respects as if it were a mixture of three different acids of different degrees of activity.

256. Degree of Dissociation from Freezing-point Data.—The freezing point of a solution sometimes informs us what proportion of the dissolved material is dissociated into ions, and what proportion persists as molecules– in other words, the **degree of dissociation.** It turns out that **as more and more water is added to a solution of an electrolyte, more and more of the dissolved molecules are dissociated into ions.**

For a substance such as NaCl, one molecule of which can furnish two ions, the freezing point lowering for a very dilute solution should approach but never exceed twice that obtained with a solution containing the same fraction of a mole of a non-electrolyte (such as sugar) in a liter. But $CaCl_2$, one molecule of which can furnish three ions, ought to give a lowering of the freezing point, in very dilute solution, approaching, but never exceeding three times the normal lowering; and one of $K_3[Fe(CN)_6]$ which can furnish four ions, a lowering approaching, but never exceeding, four times the normal one.

Experiments made with extreme care, using instruments capable of measuring temperature differences of a few ten-thousandths of a degree, have confirmed these anticipations. We have here one of the strongest arguments supporting the ionic theory, *for extremely dilute solutions.*

But it must be admitted that the results for rather concentrated solutions are quite irregular, for reasons not yet well understood. Perhaps, the simple dissociation of molecules into ions, uncomplicated by other phenomena, will be found in the end to occur only in very dilute solutions—just as the simple gas laws (§ 20) are accurately true only for highly rarefied gases.

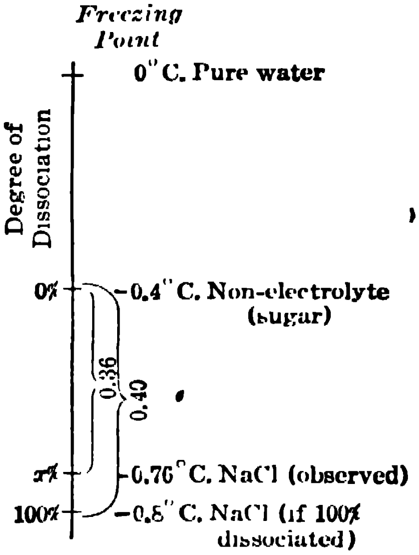
257. A Problem Based on Freezing-point Data.—For the elementary student it is of less importance to understand how to calculate degrees of dissociation from freezing-point data than it is to remember that such calculations can be made if one has need to do it.

The method is indicated in the annexed diagram. Let a solution of sodium chloride be assumed to freeze at −0.76° C. This is x per cent dissociation.

Let the freezing point of a solution containing *the same fraction of a mole* of a non-electrolyte, such as cane sugar, in the given volume of solution be −0.4°. This represents 0 per cent dissociation.

If the NaCl were completely dissociated, each molecule furnishing two ions, the freezing point would go down twice as far as with the non-electrolyte, or to −0.8° C. This represents 100 per cent dissociation.

It is now plain from the diagram that the actual dissociation of the sodium chloride is less than 100 per cent in the ratio of 0.36 to 0.40. The required degree of dissociation is therefore $0.36/0.40 \times 100 = 90$ per cent   *Ans*


Freezing Point
0° C. Pure water
Degree of Dissociation
0%
−0.4° C. Non-electrolyte (sugar)
0.36
0.40
x%
−0.76° C. NaCl (observed)
100%
−0.8° C. NaCl (if 100% dissociated)

258. Degree of Dissociation from Conductivity Data.

—As a solution of an electrolyte is diluted more and more it becomes a worse and worse conductor of electricity. This is only to be expected when we consider that diluting a solution decreases the quantity of dissolved electrolyte in each cubic centimeter.

But if we make allowance for the decrease in concentration, or if we use electrodes large enough to include all the diluted material between them (as in Fig. 67) we find that increased dilution actually increases the *total conductivity*. This means that the **addition of water causes more and more of the uncharged molecules,** which play no part in conductivity, **to dissociate into ions.** This result is quite in harmony with determinations of the freezing points of very dilute solutions.

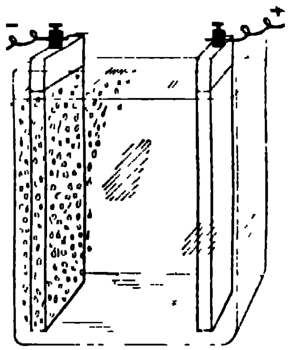


FIG. 67.

Now this total conductivity—say for one mole of dissolved substance—though it increases at first with increasing dilution, frequently reaches a maximum, after a large amount of water has been added, and thereafter remains constant. This represents 100 per cent dissociation—all the molecules of the dissolved substance dissociated into ions, and hence no possibility of forming more ions, on adding more water. If in any given case the total conductivity is just half the maximum total conductivity obtainable with the same weight of that substance in very dilute solutions, we conclude that the dissociation is 50 per cent complete.

To summarize: **Degree of dissociation may frequently be obtained by comparing total conductivity with maximum total conductivity for a given weight of a given electrolyte.**

259. General Results.—Research workers in different countries of the world, during the past forty years, have devoted a tremendous amount of labor to a study of the freezing points and conductivities of solutions in various solvents, in an attempt to discover what rules determine the extent to which different classes of substances are ionized. The results obtained have often defied interpretation. But if we limit ourselves to very dilute solutions we find that tne two chief methods agree in their testimony:

The most active acids and bases are the most completely dissociated into ions. This is presumed to indicate that **reactions between dissolved electrolytes take place between ions, rather than between molecules.** A highly ionized substance furnishes more ions than an equivalent quantity (§ 115) of a less highly ionized substance. It accordingly reacts more *rapidly* and more *completely* (§ 217) with other substances. In other words, it is more *active*. Review §§ 103, 107, 109.

Acids and bases differ widely in their degree of ionization; but **almost all salts,** with few exceptions, **are very largely ionized, regardless of whether the acids from which they are formed are active or inactive.**

DEGREE OF DISSOCIATION IN N/10 SOLUTION

About 90 per cent.	*Active acids*: HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4,* H_2CrO_4.*
	Active bases: $NaOH$, KOH.
About 80 per cent.	$Ba(OH)_2$.
65 per cent to 85 per cent.	*Most salts.*†
20 per cent to 45 per cent.	*Fairly active acids*: H_3PO_4,* H_3AsO_4,* H_2SO_3,* $H_2C_2O_4$.*
1 per cent to 10 per cent.	*Slightly active acids and bases*: HNO_2, HF, $HC_2H_3O_2$, NH_4OH.
Less than 0.2 per cent.	H_2S,* H_2CO_3.*
Less than 0.01 per cent.	HBO_2, $HAsO_2$, HCN.

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* This refers to the first (and most complete) stage of ionization of the given acid (§ 255).

† The freezing point and conductivity methods are often in poor agreement concerning the degree of dissociation of salts, especially with somewhat concentrated solutions. Some recent work shows that many salts are very largely or perhaps completely dissociated even in concentrated solutions.

260. Electronic Explanation of Ionization.—Review §§ 125, 174. The modern view of the structure of atoms helps us to understand why certain substances, when heated or dissolved, are so easily dissociated into ions. Every atom is presumed to contain a number of *external electrons* (§ 188) equal to its atomic number—two for helium, eight for oxygen, twenty-six for iron, and so forth. Chemical reactions are presumed to consist in the transfer of electrons from one atom to another, or in the association of atoms in such a way as to share certain electrons in common (Figs. 56, 57).

Now in the case of the inert gases of Group 0 these external electrons are of the proper number to form stable groups of 2, 8, 18, or 32 (§ 174); and are accordingly not readily removed or transferred to the atoms of other elements. The inert gases thus enter into no chemical reactions whatever.

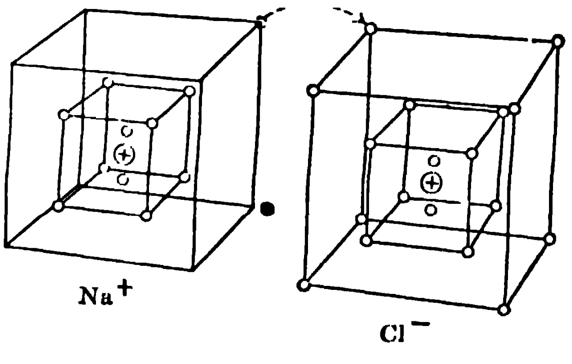
But every atom of an element of Group IA has one more electron than an atom of the preceding element of Group 0, and thus one electron too many to make a stable grouping. This extra electron (or *unit negative charge*) is readily lost, leaving the atom with a unit excess of positive electricity. Thus the electrically neutral sodium atom, Na, becomes the positive sodium ion, Na^+. Representing an electron by the symbol *e*, the process would be formulated:

$$Na \rightarrow Na^+ + e.$$

An atom of an element in Group IIA tends to lose two electrons, to revert to the stable electronic structure of an atom in Group 0. Thus we have the divalent positive ions, Mg^{++}, Ca^{++}, etc. Similarly an atom of an element in Group IIIA, by loss of three electrons, tends to form a trivalent ion, such as Al^{+++}.

Atoms of elements still further to the right may in many cases lose a correspondingly greater number of electrons and form positive ions of correspondingly higher valence. But among the heavy metals, in the middle part of the table it is often possible to reach a stable arrangement without going all the way back to Group 0. Thus iron, in Group VIII, forms Fe^{++}, Fe^{+++}, but no octavalent positive ions. Atoms of many heavy metals (such as Cr and Mn) also tend to associate themselves with oxygen and other non-metals, by sharing electrons (§ 189), to form non-metallic radicals or ions.

Atoms of elements toward the extreme right of the periodic table tend to gain electrons in sufficient number to form stable groupings. Thus an atom of sulfur, S, atomic number 16, by gaining two becomes a sulfide ion, S^{--}; and an atom of chlorine, Cl, atomic number 17, by gaining one, becomes a chloride ion Cl^-. Both of these ions have the stable grouping of 18 electrons characteristic of the next element (argon) of Group 0.



Now when we dissolve sodium chloride in water, we can see why the salt is nearly completely ionized Each sodium atom has one more electron and each chlorine atom one less electron than it needs to make a stable grouping. This electron accordingly shifts across, from sodium to chlorine, and we have Na^+ and Cl^-. These ions have something of the stable structure, and consequent chemical inertness, of atoms of the elements of Group 0. Thus they remain uncombined with each other, and are free to move off in opposite directions, if an electric current is passed through the solution.

To summarize: Atoms of metals tend to lose electrons, thus forming positive ions; and atoms of non-metals to gain electrons, thus forming negative ions. The electrons that remain are thus enabled to fall into a more stable grouping, very frequently that of an element of Group 0.

261. Some Difficulties Discussed.—

1. *Why do dissolved salts become ionized and what is the source of the electrical charges of the ions?*

If it is a crystal of NaCl which dissolves to form a solution, each sodium atom in the original crystal has probably lost an electron to a neighboring chlorine atom. Thus the sodium atom has become positively charged, and the chlorine atom negatively charged. In other words the ions Na^+ and Cl^- are already present in the crystal.

Similar remarks apply to other salts. The difficulty is not how ions are formed when certain substances dissolve in water, but why ions are not formed when electrolytes are vaporized or dissolved in all solvents whatever. At present we have no very complete or satisfying answer.

2. *How can two oppositely charged substances remain side by side in solution without neutralizing each other?*

Because they could only lose their charges by transfer of an electron from Cl^- to Na^+—a process which would require energy, since it would destroy the stable grouping of electrons (§ 189) already present in each ion.

3. *How can an electrical charge on each atom deprive chlorine of its green color?*

We do not know in detail. But if changes in valence are due to loss or gain of electrons by individual atoms (§ 133) then color must be dependent in some way on the electrical properties of atoms. For solutions of ferrous salts (Fe^{++}) are almost uniformly greenish and those of ferric salts (Fe^{+++}) almost uniformly brown; while solutions of cuprous salts (Cu^+) are colorless, and those of cupric salts (Cu^{++}) blue.

4. *How can Na^+ remain dissolved in water, without reacting with it to liberate hydrogen?*

Metallic sodium is so reactive because of its tendency to transfor electrons to the hydrogen ions of water, transforming the latter into hydrogen atoms:

Na loses one electron to form Na^+.

H^+ gains this electron and becomes H.

Then 2H unite to form H_2.

But the Na^+, formed by dissolving NaCl, has already parted with this electron, and is accordingly without effect on water.

262. Summary.

THE IONIC THEORY

Facts Supporting Theory	*Interpretation of these Facts*
1. Acids, bases, and salts, in solution, readily exchange atoms or groups of atoms.	1. Molecules of acids, bases, and salts easily decomposed into smaller fragments.
2. Freezing points of aqueous solutions of acids, bases, and salts unexpectedly low.	2. An unexpectedly large number of dissolved particles present. Many molecules broken up, by dissolving them, forming ions
3. Aqueous solutions of acids, bases, and salts conduct the electric current.	3. Ions carry electric charges.
4. Metals migrate toward *negative* electrode (cathode) during electrolysis.	4. Metallic ions (cations) carry *positive* charges.
5. Non-metals migrate toward *positive* electrode (anode) during electrolysis.	5. Non-metallic ions (anions) carry *negative* charges.
6. Quantity of electricity needed to separate a gram-atom of any element proportional to its valence (Faraday's Law).	6. Charge on each ion proportional to valence of corresponding element or group.
7. Solutions of acids, bases, and salts, in a few other solvents than water, conduct the electric current.	7. Water not the only solvent capable of dissociating molecules into ions.
8. Molten salts and alkalies conduct.	8. Heat dissociates certain molecules into ions.

General Statement of Ionic Theory.—Molecules of acids, bases and salts, when dissolved in water—or in any one of a few other (polar) solvents—are in part dissociated into electrically charged fragments of molecules, called ions. These have all the properties of ordinary molecules, and in addition certain special properties due to their electrical charges.

Some Typical Cases of Ionization.—Ionization (or electrolytic dissociation) may always be formulated as a reversible reaction.

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{+++} + 3SO_4^{--},$$

All acids yield H^+ ions.

All bases yield OH^- ions.

Degree of Dissociation.—Defined as the fractional part of the molecules in a solution dissociated into ions.

Measured—

(*a*) By comparing the freezing-point lowering with that produced by the same weight of the same substance, when completely dissociated.

(*b*) By comparing the electrical conductivity with the maximum conductivity given by the same weight of electrolyte in a very dilute solution.

Found to be—

(*a*) Greatest for salts, active acids, and active bases.

(*b*) Least for comparatively inactive acids and bases.

Electronic Explanation of Ionization. Metallic atoms tend to lose electrons and become positively charged.

Non-metallic atoms tend to gain electrons and become negatively charged.

Applications.— Summarized in § 277.

EXERCISES

1. Define and illustrate: electrolyte, electrolytic dissociation, aqueous solution, molar solution, normal solution, degree of dissociation.

2. From the following data calculate the degree of dissociation of each substance in solutions of the concentration given:

	Grams per liter.	Lowering of Freezing-point.
Acetone, $(CH_3)_2CO$	5.851	0.1875
Potassium chloride............	0.7632	0.03674
Barium chloride....	2.08	0.05
Potassium ferricyanide (§ 256). .	3.41	0.0610

3. Explain the relationship [illegible]ween conductivity and degree of dissociation.

4. Write equations to represent the electrolytic dissociation of hydrocyanic acid, nitric acid, ammonium hydroxide, ammonium sulfate, indicating which of the two component reactions predominates in each case.

5. What reaction does an aqueous solution of sodium fluoride have toward litmus? What does this show concerning the relative degrees of dissociation of NaOH and HF?

6. Formulate the electrolytic dissociation of orthophosphoric acid in three stages.

7. Which of the following are electrolytically dissociated when dissolved in water? Formulate.

Nitric acid, alcohol, lead chlorate, nitrogen, aluminum chloride, hydrogen gas, chlorine gas, potassium hydroxide, cane sugar.

8. Formulate the electrolytic dissociation of each of the following, indicating the relative completeness of the dissociation in the usual way: hydrogen sulfide, ferrous bromide, carbonic acid, sodium carbonate.

9. In the case of a solution of potassium nitrate in water, what are the principal reasons for believing: that the molecules of solute are largely dissociated into fragments of molecules; that these fragments are electrically charged.

10. State several respects in which a solution of bromine differs in its properties from one of bromide-ion. One of hydrogen gas from one of hydrogen-ion.

11. Distinguish between a test for chlorine and a test for chloride-ion.

12. Show that the generalization of § 199 is equivalent to the statement: When chlorine serves as an oxidizing agent it is changed to chloride-ion

13. Write names and formulas of the *anions* furnished by acids of § 103, and the *cations* furnished by the bases of § 107.

CHAPTER XX

SOME APPLICATIONS OF THE IONIC THEORY

263. Properties of Dissolved Electrolytes are Properties of Ions.—The sour taste of the most active acids, and their effect on indicators are properties of hydrogen-ion,* H^+, which all acids furnish when dissolved in water. Similarly, the properties common to all bases are those of hydroxyl-ion, OH^-. The differences in degree of activity among acids and bases are ascribed to differences in the degree of completeness with which they are dissociated into ions when dissolved in water (§ 259). Again, hydrochloric acid and all metallic chlorides yield a precipitate with silver salts (§ 186) because they all furnish chloride-ion, Cl^-, which by union with silver-ion, Ag^+, forms molecules of silver chloride; and sulfuric acid and all metallic sulfates yield a precipitate with barium salts because they all furnish sulfate-ion, SO_4^{--}, which by union with barium-ion, Ba^{++}, forms molecules of barium sulfate. Thus **the properties of dissolved electrolytes are in general properties of ions; and the *tests* applied in analytical chemistry for the identification of different classes of dissolved electrolytes are really tests for the different kinds of ions which these electrolytes furnish.** Silver-ion, Ag^+, serves as a test for chloride-ion, Cl^-; barium-ion, Ba^{++}, as a test for sulfate-ion, SO_4^{--}; and conversely.

264. Ionic Formulation of Double Decomposition.—Review § 129. When potassium nitrate and sodium chloride are dissolved separately in water, they are both very largely dissociated into ions (reactions *a*, *b*):

$$\begin{array}{ccccc}
\mathrm{KNO_3} & \overset{a}{\rightleftarrows} & \mathrm{K^+} & + & \mathrm{NO_3^-}\\
 & & + & & +\\
\mathrm{NaCl} & \overset{b}{\rightleftarrows} & \mathrm{Cl^-} & + & \mathrm{Na^+}\\
 & & e \uparrow\downarrow c & & f \uparrow\downarrow d\\
 & & \mathrm{KCl} & & \mathrm{NaNO_3}
\end{array}$$

---

* *Hydrogen-ion* (written with a hyphen) is a substance (§ 9); *hydrogen ions* are the individual, electrically charged particles that compose it.

On mixing the two solutions, there is a chance for cross-combination (*c*, *d*) among the four kinds of ions. But actually very little happens (*c* and *d* are dotted arrows) because the anticipated products, KCl and $NaNO_3$, have about as great a tendency (*e*, *f*) as the original pair of salts to remain in the form of ions. The absence of any noteworthy reaction is also indicated by the fact that there is no appreciable liberation or absorption of heat when the two solutions are mixed.

In general: **Double decomposition between dissolved electrolytes fails to occur when both the expected products are largely ionized and freely soluble.**

265. Ionic Formulation of Precipitation.—If one of the expected products is slightly soluble something happens. If we take solutions of silver nitrate and sodium chloride, each substance is largely ionized (reactions *a*, *b*) before the solutions are mixed. On mixing there is opportunity for cross-combination (*c*, *d*).

$$\begin{tikzcd}
\text{AgNO}_3 \arrow[r, shift left, "a"] & \text{Ag}^+ \arrow[l, shift left] & + & \text{NO}_3^- \\
 & + & & + \\
\text{NaCl} \arrow[r, shift left, "b"] & \text{Cl}^- \arrow[l, shift left] \arrow[d, shift left, dashed] & + & \text{Na}^+ \arrow[d, shift left, dashed] \\
 & \underset{\text{(Dissolved)}}{\text{AgCl}} \arrow[u, shift left, "c"'] \arrow[d, shift left] & & \text{NaNO}_3 \arrow[u, shift left, "d"'] \\
 & \underset{\text{(Precipitated)}}{\text{AgCl}} \arrow[u, shift left, "e"'] & &
\end{tikzcd}$$

But note especially that **Na^+ and NO_3^- do not unite to any very considerable extent** (reaction *d*) because $NaNO_3$ is about as completely ionized as the original pair of salts. But reaction *c* becomes practically complete, because AgCl is very slightly soluble, and is removed by precipitation (reaction *e*) almost as fast as formed (§ 68) Thus **practically the only chemical change taking place is:**

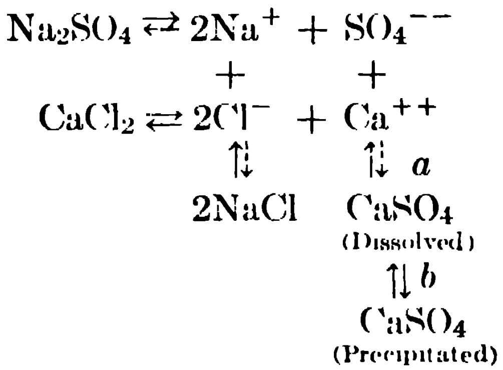
$$Ag^+ + Cl^- \longrightarrow AgCl \text{ (mostly precipitated).}$$

The double decomposition has turned out to be a case of *direct union*, and no exchange of atoms (§ 113–4) at all.

But note that a very small amount of silver chloride—about

1.6 mg. per liter—still remains dissolved at the end of the precipitation, and *practically all as ions*, Ag^+ and Cl^-.

266. How to Make a Precipitation as Complete as Possible.—If we add a dilute solution of sodium sulfate to one of calcium chloride, a precipitate of *calcium sulfate* is formed:



$$\begin{array}{rcl}
\mathrm{Na_2SO_4} \rightleftarrows & \mathrm{2Na^+} & + \ \mathrm{SO_4^{--}} \\
 & + & \quad + \\
\mathrm{CaCl_2} \rightleftarrows & \mathrm{2Cl^-} & + \ \mathrm{Ca^{++}} \\
 & \updownarrow & \quad \updownarrow a \\
 & \mathrm{2NaCl} & \quad \mathrm{CaSO_4} \\
 & & \quad \text{(Dissolved)} \\
 & & \quad \updownarrow b \\
 & & \quad \mathrm{CaSO_4} \\
 & & \quad \text{(Precipitated)}
\end{array}$$

But $CaSO_4$ is much more soluble than the precipitate (AgCl) considered in § 265. In fact, a liter of pure water may be made to dissolve about 2 g. of $CaSO_4$; mostly, of course, as Ca^{++} and SO_4^{--} ions. Accordingly the precipitation of $CaSO_4$, as formulated above, is commonly not quite complete. But it may be made more nearly complete by adding to the solution an excess of Na_2SO_4, which would bring into the reaction extra SO_4^{--} ions; or by adding an excess of $CaCl_2$, which would bring in extra Ca^{++} ions. In either case reaction *a* would be favored (Law of Mass Action, § 217) resulting in an accumulation of $CaSO_4$ molecules in a solution already saturated with respect to that salt. The result is a slight additional precipitation of $CaSO_4$ crystals (reaction *b*)

Thus, in general: **To make a precipitation as complete as possible, it is necessary to add a slight excess of one of the ions concerned in the formation of the precipitate.** Usually an excess amounting to a few drops of the precipitating solution will be sufficient. **Any very large excess should usually be avoided,** for reasons to be discussed later (§ 536).

Give an ionic formulation of the interaction of ammonium iodate and silver nitrate, to produce a precipitate of silver iodate. Indicate two different ways of causing this precipitation to become more complete.

Name two ions, either of which is capable of decreasing the solubility of the slightly soluble substance, CaC_2O_4, in pure water. Name several salts, any one of which would cause some solid calcium oxalate to separate when added to a saturated solution of that salt.

267. The Ionization of Water.—Water that has been very carefully purified by repeated distillations proves to be a fairly good insulator. But it does let some current through, in spite of all attempts to free it from traces of dissolved substances. The conclusion is that **water is itself dissociated to a very slight extent, yielding hydrogen ions, H^+, and hydroxyl ions, OH^-.**

Measurements of the conductivity of the purest water ever obtained indicate that *at room temperatures* it contains only 1 gram-ion (=1.008 g.) of H^+ and 1 gram-ion (=17.008 g.) of OH^- in ten million liters! From this we may calculate that **only about one molecule of water in 500,000,000 is dissociated into ions at ordinary temperatures.**

These H^+ and OH^- ions, few as they are, are of great importance. For they appear to be responsible for numerous reactions of practical interest (§ 113) in which water plays a part. Without them, water would probably be as inactive chemically as benzene.

It is important to remember that in terms of the ionic theory **a neutral solution is one containing H^+ and OH^- ions in the same concentration as in water—one ten-millionth ($=10^{-7}$) gram-ions of each in 1 liter.** An acid solution contains an excess of hydrogen-ion (H^+); and an alkaline solution an excess of hydroxyl-ion (OH^-). But note that **OH^- ions are not altogether absent in an acid solution, nor H^+ ions in an alkaline solution.** As the concentration of H^+ increases, that of OH^- must decrease, and *vice versa*, the product of the two concentrations remaining the same as in pure water (in which it is $10^{-7} \times 10^{-7} = 10^{-14}$).

Thus, a solution of N/100 acid (§ 177), assumed to be completely ionized, contains $1/100 = 10^{-2}$ g.-ions of H^+ per liter. The concentration of OH^- is therefore 10^{-12}.

268. Neutralization.—Review §§ 112 and 267. From the point of view of the ionic theory, **an acid is anything that can furnish H^+ ions, and a base anything that can furnish OH^- ions, when dissolved in water.** A few substances can ionize in two different ways, furnishing either H^+ or OH^-, as occasion may demand (§ 473).

If HCl and NaOH are dissolved separately in water to make dilute solutions, each substance is very largely dissociated into ions (reactions *a* and *b*):

$$\begin{tikzcd}[row sep=small]
HCl \arrow[r, shift left, "a"] & H^+ \arrow[l, shift left] & + & Cl^- \\
 & + & & + \\
NaOH \arrow[r, shift left, "b"] & OH^- \arrow[l, shift left] \arrow[d, shift left, "d"] & + & Na^+ \arrow[d, shift left, "c"] \\
 & HOH \arrow[u, shift left] & & NaCl \arrow[u, shift left]
\end{tikzcd}$$

When the two solutions are mixed, a very few Na^+ and Cl^- ions unite to form NaCl molecules (reaction *c*); for NaCl is about as completely ionized in dilute solution as the original acid and base. Water is but slightly ionized; hence nearly all the H^+ and OH^- ions unite to form molecules of water (reaction *d*). The removal of these ions favors reactions *a* and *b*, already almost complete. Thus, if acid and base are employed in equivalent quantities, the solution in the end will contain only HOH, Na^+, and Cl^-, with a very small amount of undissociated NaCl molecules.

Thus, from the point of view of the ionic theory, **neutralization consists in the union of H^+ ions from an acid with OH^- ions from a base, to form molecules of water. The other ions furnished by the acid or base**—Cl^- and Na^+, in the illustration above—**remain for the most part uncombined.**

Give an ionic formulation of the neutralization of acetic acid by ammonium hydroxide. Explain why the neutralization is almost complete, in spite of the fact that both these substances are but slightly ionized when dissolved in water.

269. Hydrolysis.—Review §§ 113, 114. A solution of sodium fluoride in water reacts alkaline toward litmus. We have explained this by saying that although NaOH and HF are produced by the hydrolysis of this salt in equal amounts, still the former, being the more *active*, has the *predominating effect* on litmus.

But with the help of the ionic theory we are able to explain why only the salts of inactive or insoluble acids or bases are hydrolyzed; and why a solution of a partially hydrolyzed salt may react acid toward one indicator and alkaline toward another.

Let us take sodium fluoride for our example. This, being a salt, is almost completely ionized (reaction *a*) into Na^+ and F^-. The water itself furnishes a very few H^+ and OH^- ions (reaction *b*).

The four ionic products then interact (reactions *c* and *d*) giving a final result which may be formulated:

$$\begin{array}{ccccc} \text{NaF} & \overset{a}{\rightleftarrows} & \text{Na}^+ & + & \text{F}^- \\ & & + & & + \\ \text{HOH} & \overset{b}{\rightleftarrows} & \text{OH}^- & + & \text{H}^+ \\ & & \uparrow\downarrow c & & \uparrow\downarrow d \\ & & \text{NaOH} & & \text{HF} \end{array}$$

Since NaOH is an active (largely ionized) base, equilibrium can be established without withdrawing many OH^- ions, in reaction *c*, to form NaOH molecules. But HF is a slightly active (slightly dissociated) acid. Accordingly, a good many H^+ ions are withdrawn, in reaction *d*, to form HF molecules, before equilibrium can be established.

But since H^+ and OH^- are furnished in equal quantities by reaction *b*, it is plain that the withdrawal of the comparatively large quantity of H^+ in reaction *d* will leave the solution with an excess of OH^-. In other words, a solution formed by dissolving NaF in water reacts *alkaline*.

In the contrary case, with such a salt as ammonium chloride, the base being inactive and the acid active, there remains in the end an excess of H^+ over OH^- ions, and the solution reacts *acid*, toward sufficiently sensitive indicators. Give the detailed formulation.

In general: **Hydrolysis consists in the union of the ions of a dissolved salt with unequal quantities of the H^+ or OH^- ions of water, to form molecules of an inactive acid or base.**

Any salt derived from an acid or base of very different degree of activity will furnish a slightly alkaline or acid solution when dissolved in water.

Write ionic formulations for one example of each of the four types of salts listed in § 117, and explain the effect of the solution on indicators.

270. Four Cases in Which Double Decomposition is Complete.—Review § 136. We have learned that double decomposition between dissolved electrolytes is complete whenever—

1. *A precipitate is formed.* Such a reaction involves a *direct union* of ions to form molecules of a slightly soluble substance.

$$Ag^+ + Cl^- \longrightarrow AgCl \text{ (precipitated) } \S\, 265.$$

2. *A gas is evolved.*

Thus, when a solution of sodium chloride is evaporated with an excess of dilute sulfuric acid, we have:

$$\begin{tikzcd}
H_2SO_4 \arrow[r, shift left, dashed] & H^+ \arrow[l, shift left] & + & HSO_4^- \\
 & + & & + \\
NaCl \arrow[r, shift left, dashed, "b"] & Cl^- \arrow[l, shift left] \arrow[d, shift left, dashed, "c"] & + & Na^+ \arrow[d, shift left, dashed, "d"] \\
 & \underset{\text{(Dissolved)}}{HCl} \arrow[u, shift left, "c"] \arrow[d, shift left] & & NaHSO_4 \arrow[u, shift left] \\
 & \underset{\text{(Gas)}}{HCl} \arrow[u, shift left] & &
\end{tikzcd}$$

Reaction *c* here becomes nearly complete because the HCl molecules produced are for the most part vaporized with the evaporating water. But if the evaporation is discontinued before $NaHSO_4$ begins to crystallize out, a fair amount of HCl does remain dissolved; and since most of it is present as ions rather than as molecules, reaction *c* is represented by a dotted arrow, and *e* by a heavy one.

The principal chemical change in this reaction is *direct union*:

$$H^+ + Cl^- \rightarrow HCl \text{ (expelled as a gas).}$$

3. *A slightly active acid or base is formed.*

When hydrochloric acid is added to a solution of sodium acetate, it is almost completely converted into acetic acid. The reaction is *direct union* of hydrogen-ion from the hydrochloric acid with acetate-ion from the sodium acetate:

$$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2.$$

Formulate this in detail, as in the preceding case, taking care to distinguish degrees of ionization by dotted and heavy arrows.

4. *An active acid neutralizes an active base.*

This again is a *direct union*,

$$H^+ + OH^- \rightarrow HOH \text{ (§ 268).}$$

It may be asked why direct union of H^+ and OH^- to form molecules of water is not always complete, whether the acid and base concerned are active or inactive. The answer is that the neutralization is carried out in *aqueous solution*, in the presence of a huge excess of water, which favors the reverse reaction—hydrolysis (Law of Mass Action, § 217). Only if the acid and base concerned are both relatively active, or if the reaction is carried out in some other solvent than water, is neutralization practically complete, and hydrolysis practically absent.

To summarize: **A reaction of double decomposition between dissolved electrolytes is practically complete only when a precipitate, gas, or slightly ionized substance is formed, or when water is produced by the action of an active acid on an active base.**

The principal chemical change in double decomposition always consists in the direct union of ions to form molecules of a precipitated or slightly ionized substance.

271. Why Indicators Change Color.—The two different colors shown by an indicator correspond to two different arrangements of atoms within its molecule. One of the two forms appears always to have the nature of an inactive acid or base; that is, it dissociates to a very slight extent, furnishing H^+ or OH^- ions. The other form is in comparison *practically non-ionized.*

If we represent the non-ionized form of an indicator-acid (such as phenolphthalein) by (HX) and the ionized form by H.X the equilibrium existing in a solution of the indicator in water may be formulated.

$$(HX) \quad \overset{b}{} \quad H.X \qquad + \quad X^-$$

(Obtained in
acid solution)

Ions of indicator
salt
(Obtained in
alkaline solution)

It is plain that adding a base to a solution containing the indicator will remove H^+, and thus favor reaction *a*. The decrease in the concentration of H.X will then favor reaction *b*. Thus in the end, practically all the (HX) will disappear, and the solution will show the color characteristic of the ions, X^-, of the indicator salt. But the addition of an acid, i.e., H^+, to the solution favors the reverse reactions, *c* and *d*, and causes both X^- and H.X largely to disappear. The solution then shows the color characteristic of the non-ionized form, (HX).

The actual concentration of hydrogen-ion, H^+, which must be present in order to cause a change in color will of course depend on whether a solution of the indicator in pure water is predominantly (HX) or H.X, on the activity (i.e., tendency to ionize) of H.X, and on the relative intensities of the two colors.

Each given indicator changes color in the presence of a definite slight excess of acid or base, and commonly not in a precisely neutral solution.

272. Choice of Indicators.—It is common to think of indicators, in a hazy sort of way, as substances having one color in an acid and another in an alkaline solution. This has served well enough for a preliminary definition (§ 102; but we have just seen that the change in color does not occur when the solution is precisely neutral.

An indicator should actually change color when acid and base have been brought together in chemically equivalent quantities—one gram-equivalent of acid for one gram-equivalent of base. *But the solution thus obtained will not be strictly neutral unless both acid and base are of the same activity* (§ 114). Thus, on neutralizing chemically equivalent quantities of NaOH and HF, the solution of NaF obtained still reacts alkaline to litmus, due to hydrolysis (§ 269). *If the titration were continued until the solution became neutral to litmus we should have too much acid.*

Three different types of indicators must thus be used, in very careful work, according to the relative activities of acid and base:

1. **Active acid and inactive base.** Use an indicator which changes color when the solution has a slight excess of H^+ over OH^- ions (a faintly acid solution). *Methyl red* and *methyl orange* are perhaps the most useful.

2. **Inactive acid and active base.** Use an indicator which changes color when the solution has a slight excess of OH^- over H^+ ions (a faintly alkaline solution). *Phenolphthalein* or *thymol blue.*

3. **Active acid and active base.** Use any indicator if CO_2 of atmosphere is excluded. Otherwise use one sensitive only to active acids and therefore not affected by H_2CO_3. *Methyl red* or *methyl orange.*

4. **Inactive acid and inactive base.** No indicator will give good results.

Hundreds of other indicators are known. The most useful of these are artificial organic substances, of complex composition. But in the early days of chemistry a number of rather inferior natural indicators were pressed into service: the juice of red cabbage leaves, coffee, or alcoholic extracts of colored blossoms or the cochineal insect of Central America. Litmus—furnished by a species of lichen—is still in general use, but is too variable in quality to deserve consideration in the most accurate work.

273. Total, Momentary, and Reserve Acidity.—A liter of N/10 hydrochloric acid is chemically equivalent to a liter of N/10 acetic acid, in the sense that each will neutralize the same quantity of a base. This is expressed by saying that **equal volumes of**

N/10 hydrochloric acid and N/10 acetic acid have the same *total acidity*.

Total acidity is determined by the total amount of replaceable hydrogen in the solution, as acid molecules and hydrogen ions.

The total acidity of a solution can be measured by titrating the solution with a base (§ 115); for, as the H^+ ions of the acid are removed to combine with the OH^- ions of the base, other H^+ ions are formed to take their place, by the dissociation of acid molecules. Thus in the end both H^+ ions and acid molecules disappear.

2. There are several respects, however, in which hydrochloric acid and acetic acid are far from interchangeable. (*a*) If the solutions are of the same concentration (say both N/100) the hydrochloric acid will have a sourer taste. If the two acids compete for a limited quantity of a base or a metal, the hydrochloric acid wins, and leaves most of the acetic acid uncombined. (*b*) A solution of hydrochloric acid is a much better conductor of the electric current than acetic acid, and (*c*) a much better catalytic agent in certain reactions to be studied hereafter (§ 366).

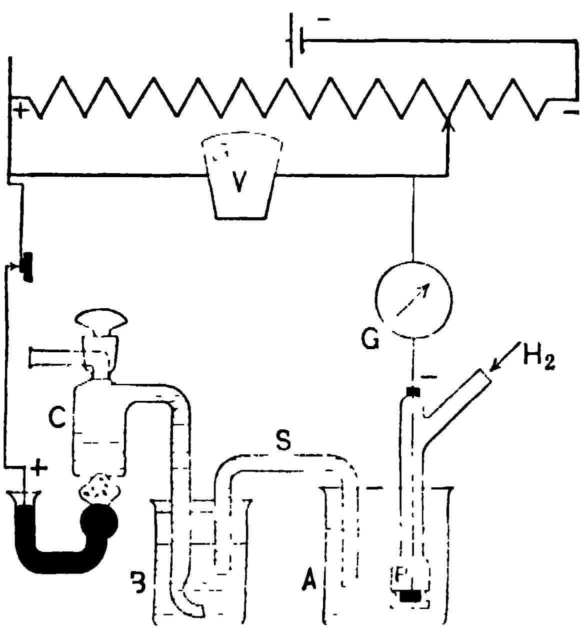


FIG. 68.—Determination of momentary acidity, or hydrogen-ion concentration, with a hydrogen electrode. The hydrogen electrode, *P*, consists of a sheet of gold or platinum, coated with finely divided platinum or palladium, which is saturated with hydrogen gas. When this is connected with a "calomel electrode" (*C*) an electric current tends to flow, the intensity (electromotive force) of which depends on the hydrogen-ion concentration of the solution into which the hydrogen electrode dips. See textbooks of Physical Chemistry.

These facts are explained by saying that **such characteristically acid properties as sour taste or chemical activity in uniting with bases or metals, are due to H^+ ions rather than to acid molecules (§ 263). Thus the concentration of the hydrogen ions in a solution measures what has been called its *momentary acidity*.**

Momentary acidity may be estimated roughly by the sourness of a solution. Strawberry juice tastes sourer than tomato juice because it has a greater momentary acidity. But titration with a base would show the tomato juice to have the greater total acidity.

Momentary acidity may also be estimated by measuring the conductivity of the solution (if salts are absent), but a more accurate and convenient method is that which makes use of the *hydrogen electrode* (Fig. 68).

3. The difference between the total and momentary acidity of a solution is called its **reserve acidity.** Thus, the differences between the properties of the two acids we have just discussed may be summarized as follows:

$$\begin{array}{ccccc} \underset{\substack{\text{Low}\\ \text{reserve}\\ \text{acidity}}}{HCl} & \rightleftarrows & \underset{\substack{\text{High}\\ \text{momentary}\\ \text{acidity}}}{H^+} & + & Cl^-; \\ \underset{\substack{\text{High}\\ \text{reserve}\\ \text{acidity}}}{HC_2H_3O_2} & \rightleftarrows & \underset{\substack{\text{Low}\\ \text{momentary}\\ \text{acidity}}}{H^+} & + & C_2H_3O_2^-; \end{array}$$

when the total acidities are equal.

274. Repression of Ionization by a Common Ion.—Acetic acid is but slightly dissociated (reaction *a*) even in dilute solution:

$$HC_2H_3O_2 \underset{b}{\overset{a}{\rightleftarrows}} H^+ + C_2H_3O_2^-.$$

By adding sodium acetate—which, like nearly all other salts, is very completely ionized to an acetic acid solution, we bring into the latter a large extra supply of acetate-ion, $C_2H_3O_2^-$. The result of this, by the Law of Mass Action (§ 217) is to favor reaction *b* in the equilibrium formulated above. Thus, the small momentary acidity (H^+) of the acetic acid is still further decreased, and its reserve acidity ($HC_2H_3O_2$) further increased, while the total acidity remains practically unchanged. A tenth-normal solution of acetic acid, by the addition of a little sodium acetate, may have its momentary acidity so far reduced as actually to become alkaline to such an indicator as methyl orange; while its total acidity, as measured by the alkali which it can neutralize in titration, remains practically as large as before.

The same principle may be applied in many other cases: **The degree of ionization of any *inactive* acid or base is always decreased by the addition of salts having *an ion in common with itself***—acetates to acetic acid; carbonates to carbonic acid, etc.

This important principle finds many applications in analytical chemistry, when it is desired to prepare a solution of a definite but limited H^+ or OH^- concentration. The degree of ionization of an *active* acid or base, such as HCl or NaOH, is not appreciably affected by the addition of any of its salts.

275. Buffer Salts and their Practical Applications.—It can be shown that sodium acetate not only decreases the H^+ concentration of acetic acid but *stabilizes* it, protecting it to some extent against alterations due to addition of alkalies or to dilution. **Salts which tend to hold the H^+ or OH^- concentration of a solution to a definite value are called buffer salts. Acid solutions are buffered with salts of inactive acids** ($NaC_2H_3O_2$ or Na_2HPO_4), **basic solutions by salts of inactive bases** (NH_4Cl).

Buffer salts play a very important rôle in nature. Most of the juices of ordinary fruits and vegetables have a definite, though slight, acidity, which is held very constant by the action of buffer salts contained in the juices.

The blood has a definite, though very faint, alkalinity, which it maintains with the greatest precision, in part through the action of buffer salts. Solutions to be injected intravenously by physicians must be properly buffered before being heated in an autoclave to sterilize them.

Pure cultures of acid-resisting forms of yeast are cultivated in solutions buffered to a definite acidity. Faint acidity, properly buffered, may also be used to supplement heat, as a means of sterilization.

276. The Hydrogen-Ion Index.—It is customary to express extremely faint acidities and alkalinities in **pH-values,** sometimes called **hydrogen-ion indexes.** The *p*H-value of a solution is the logarithm of the number of liters that must be taken to contain one gram-ion of hydrogen. In the case of pure water, this is ten million liters (§ 267). But log 10,000,000 = 7. Accordingly, the *p*H-value of water or any neutral solution is 7. Acid solutions have a *p*H-value less than 7; and alkaline solutions greater than 7. Thus, the *p*H-value of normal human blood is 7.5.

What is the *p*H-value of $\frac{N}{100}$ acid, assuming it to be completely ionized?

277. Summary.

APPLICATIONS OF THE IONIC THEORY

Properties of solutions of electrolytes are properties of ions.

Double Decomposition.

Incomplete when expected products are both freely soluble and largely ionized (§ 264).

Complete when a precipitate, gas, or slightly ionized substance is formed, or when an active acid neutralizes an active base (§ 270).

Consists in the *direct union* of ions to form molecules of the slightly soluble or slightly ionized substance.

Precipitation.

One of the four cases of complete double decomposition. In the case of appreciably soluble salts, precipitation becomes more nearly complete in the presence of an excess of one of the two ions concerned in the formation of the molecules of precipitate.

Ionization of Water.

About one molecule of water in 500,000,000 dissociated into H^+ and OH^- at ordinary temperatures (§ 267).

Neutralization.

Consists in the union of H^+ and OH^- ions to form molecules of water (§ 268).

Hydrolysis.

Consists in the unequal withdrawal of the H^+ and OH^- ions of water to form molecules of a slightly dissociated acid or base (§ 269).

This effect determines the choice of an indicator (§ 272).

Total, Momentary, and Reserve Acidity (§ 273).

1. *Total acidity* is measured by total replaceable hydrogen in H^+ ions and acid molecules. Determined by titration with a base.

2. *Momentary acidity* (=hydrogen-ion concentration) is measured by H^+ ions present in the solution at any moment in equilibrium with undissociated acid molecules.

Determined by hydrogen electrode.

3. *Reserve acidity* is the difference between total and momentary acidity.

Buffer Salts.

Salts containing an ion in common with the given slightly active acid:

1. Decrease the hydrogen-ion concentration of the acid solution (§ 274).

2. Buffer, or protect it, against the influence of slight amounts of alkali (§ 275).

Process of Dissolving a Metal in an Acid.

Consists in the transfer of electrons from the metallic atoms to hydrogen ions of the solution (§ 276).

Complex Ions (to be discussed in §§ 421, 535, 536, 543, 544).

Primary cells (§ 425).

Electrolysis (§§ 426, 427).

EXERCISES

1. Give a complete ionic formulation of the formation of calcium oxalate (insoluble) by a double decomposition between two soluble salts.

2. Give a complete ionic formulation of a double decomposition between lead acetate and potassium iodide, precipitating lead iodide.

3. Give an ionic formulation to explain why a solution of ferric chloride turns blue litmus red.

4. How many milligrams of hydrogen-ion in a liter of pure water at 18° C.? How many milligram-equivalents?

5. Explain how the relative activities of acids and bases may be determined from the reactions of salt solutions toward indicators.

6. Mention two other methods for determining relative activity.

7. Give an ionic formulation to explain the reaction of a solution of sodium carbonate toward litmus.

8. Estimate the approximate hydrogen-ion concentrations, in gram-equivalents per liter, of each of the following: pure water; normal NaCl;

N/10 acetic acid, assumed 1 per cent ionized; N/1000 NaOH, assumed completely ionized; 10N H_2SO_4, assumed 50 per cent ionized (first stage) and 10 per cent ionized (second stage); N/1000 HCl, assumed completely ionized.

9. What is the pH value of each of the solutions just mentioned?

10. Estimate, roughly, the total, momentary, and reserve alkalinities, in gram-ions of OH^- per liter, of a N/10 solution of NH_4OH.

11. Explain why different indicators are needed in the titration of different acids. Give the general rules which determine a choice in any particular case.

12. State which class of indicators you would use in each of the following titrations, and why:

H_2SO_4 and NH_4OH;
H_2S and KOH;
HCN and $Ba(OH)_2$;
HI and $C_6H_5(NH_2)$ (a very slightly active base.)

13. How would you prepare a buffered solution of definite faint acidity? Of definite faint alkalinity?

14. Formulate the electrolytic dissociation of sodium bicarbonate (two steps).

15. Give an ionic formulation of the precipitation of lead acetate by hydrogen sulfide, indicating approximate degrees of ionization throughout.

16. Give molecular, ionic, and electronic formulations of the process of dissolving metallic zinc in hydrochloric acid.

17. Write the following equations in ionic form:

$$NaOH + HI = H_2O + NaI;$$
$$Pb(C_2H_3O_2)_2 + Na_2CrO_4 = PbCrO_4 \text{ (insol.)} + 2NaC_2H_3O_2;$$
$$2KBr + Cl_2 = 2KCl + Br_2;$$
$$SnCl_2 + Cl_2 = SnCl_4;$$
$$2CrCl_3 + Zn = 2CrCl_2 + ZnCl_2.$$

18. Which of the reactions in the preceding question involve oxidation and reduction? Explain each of these as a transfer of electrons.

19. Write ordinary (molecular) equations to represent the following changes: iron dissolves in an acid to form a ferrous salt; a bromide is decomposed by sulfuric acid; mercurous bromide is oxidized to mercuric bromide by bromine. Rewrite these equations in ionic form, and name the ionic substances indicated.

CHAPTER XXI

NITROGEN, AMMONIA, AND AMMONIUM SALTS

278. Importance of the Chemistry of Nitrogen.—The element nitrogen furnishes an excellent illustration of how men and women in the most diverse professions find common interests in chemistry. The biologist and the physician are interested in nitrogen because all the manifold phenomena of metabolism, growth, reproduction, and decay involve changes of this element from one state of combination to another. The architect and the civil engineer appreciate that land is cleared, building stones quarried, foundations excavated, and tunnels and canals built with the aid of high explosives—all nitrogen compounds. The farmer needs to take account of the ways in which the different forms of nitrogen in crops and soil are conserved, to win the greatest return from his acres, and reserve them for the future in undiminished fertility.

The electrical engineer should know something about the processes by which nitrogen is brought into combination with other elements, to form ammonia and nitric acid, in electric furnaces; for some of the greatest developments of electrical power within the past few years have been in connection with these industries. Finally, the statesman should understand the relation of such nitrogen compounds as ammonia, nitric acid, and dyestuffs to the national defense; and should support legislation to encourage the production of fertilizers from the nitrogen of the atmosphere, to aid in supplying foodstuffs for the nation.

279. Occurrence of Nitrogen.—1. An inexhaustible supply of **elementary nitrogen** is found in the atmosphere, which is about three-fourths nitrogen by weight. This amounts to more than 20,000,000 tons of the element for each square mile of the earth's surface.

2. Great deposits of **sodium nitrate** and **calcium nitrate** occur in various parts of the world, notably in Chile.

The Chilean sodium nitrate beds are over 200 miles long, and average 2 miles wide and 5 ft. thick. Over 50,000,000 tons of this nitrate have been exported since the deposit was discovered, something over a century ago. The present exportation is probably more than 2,000,000 tons a year. The crude material contains 20 to 60 per cent $NaNO_3$ (often called Chile saltpeter) and is recrystallized (§ 97) in great open basins, where evaporation takes place by the heat of the sun.

3. **Ammonium salts** occur in small deposits in certain of the dryer regions of the world, but are chiefly obtained from the ammonia produced in the **destructive distillation of coal** (§ 283).

4. Nitrogen is found in all plant and animal matter, in the gelatinous material called **protoplasm,** which lines the walls of living cells. Nitrogen compounds called **proteins** (§ 388) make up most of the weight of dry meat, and related substances compose gelatin, horn, feathers, and hair.

280. How the Composition of the Atmosphere is Determined.—That the atmosphere is a mixture, and not a chemical compound at all, is proved by the fact that it varies somewhat in its composition from place to place and from time to time.

Its composition by volume may be determined by absorbing its different constituents, one after the other, in different chemical reagents, measuring the decrease in volume that takes place in each case. *Carbon dioxide* is usually absorbed in potassium hydroxide solution, forming potassium carbonate:

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

Oxygen is often absorbed in an alkaline solution of pyrogallol. The reaction is complicated, and cannot be represented by a single equation.

Sticks of yellow phosphorus, in contact with water, also absorb oxygen. The phosphorus is oxidized to phosphorus trioxide and other oxides, which then combine with the water. Other good absorbents are solutions of cuprous chloride or chromous chloride ($CrCl_2$) in hydrochloric acid, alone or mixed with stannous chloride.

The portion of the air remaining unabsorbed after passing through the absorbents for carbon dioxide and oxygen consists, for the most part, of *nitrogen.* Even this may be brought into combination by passing the mixture through a tube containing heated magnesium turnings. The unabsorbed residue from this operation is largely *argon.*

On the average, the composition of dry air is found to be:

	Per Cent by Volume	Per Cent by Weight.
Nitrogen.	77 94	75.30
Oxygen.	20 95	23 15
Argon.	0 94	1 30
Carbon dioxide.	0 03	0 05
Helium, neon, etc	0 14	0 20
	100 00	100 00

If the atmosphere continued to be of uniform density as we ascended, we should find it to be about 5 miles deep. If it could then be resolved into its different constituents and separated into different layers, we should have on the surface of the earth about 5 in. of condensed water; above that a layer of carbon dioxide gas about 13 ft. deep; then a layer of argon about 90 yds. deep; a mile of oxygen; and finally 4 miles of nitrogen.

281. Preparation of Elementary Nitrogen.—1. **Commercially,** nitrogen is now prepared on an enormous scale, along with oxygen, from liquid air (§ 54).

2. **On the small scale suitable for the laboratory,** a current of nitrogen (mixed with argon) may be obtained by bubbling air through a solution containing ammonium chloride and ammonium hydroxide, in the presence of copper turnings.

The copper is oxidized, forming a blue solution of cupric ammonium hydroxide (§ 535). The gas thus obtained is, of course, passed through dilute sulfuric acid to remove ammonia, and is then freed from the last traces of oxygen by being passed over heated copper or through one of the absorbents for oxygen mentioned in the preceding section.

3. **Nitrogen free from argon** is most conveniently prepared by heating a solution of *ammonium chloride,* while a solution of *sodium nitrite* is being run in. The nitrite group (or ion), serves as the oxidizing agent (§ 135), the valence of its nitrogen decreasing from +3 to 0; and the ammonium group (or ion) serves as a reducing agent, the valence of its nitrogen increasing from −3 to 0;

$$NH_4Cl+NaNO_2=NaCl+N_2\uparrow+2H_2O.$$

Show that the nitrogen in each group really has the valence stated (§ 121). Write this reaction in ionic form.

282. Uses of Elementary Nitrogen.—The production of ammonia by the *Haber* and cyanamide processes (§ 284) calls for enormous quantities of nitrogen gas. Thus, Germany is reported to have consumed half a million tons of nitrogen each year in the cyanamide process alone, during the latter part of the Great War.

The chemical inertness of nitrogen makes it useful in the laboratory for diluting other and more active gases, in order to moderate reactions that would otherwise get out of control. It serves also to sweep the air out of apparatus in which operations requiring the exclusion of oxygen are to be carried on.

The best thermometers are filled with compressed nitrogen above the mercury thread, to reduce the error due to the evaporation of the metal at high temperatures.

283. Ammonia and Ammonium Salts from Coal and Shale.—The most important source of ammonia and ammonium salts is **coal.** When this is strongly heated in a closed retort, out of contact with air, the chemical substances it contains are decomposed, producing a mixture of volatile products, including coal-gas and tar (§ 350). Incidentally, the complex compounds of nitrogen contained in the coal are transformed into simpler ones, of which ammonia is the most important.

The gas from the retorts is passed through a tar-separator, then into dilute sulfuric acid, which removes the ammonia to form ammonium sulfate. The United States now produces about 500,000 tons of this salt each year, and permits about an equal amount to be wasted. Oil shale (p 310) also contains a considerable quantity of combined nitrogen; in Scotland, the ammonia that it yields often pays the entire cost of the distillation process.

284. Synthetic Ammonia.—During the Great War, a number of processes for synthesizing ammonia from its elements were perfected and put into operation on a large scale, to supplement ammonia from coal. The ability of Germany to hold out for four years, when cut off from supplies of nitrogen compounds from overseas, is directly attributable to her success in developing synthetic ammonia and oxidizing this to nitric acid, for preparation of explosives. Of the several methods for synthesizing ammonia that have been used, we shall describe two.

1. **Direct Synthesis.**—If nitrogen and hydrogen are brought together under a pressure of about 200 atmospheres, at 500° C. in a reaction chamber (*A*, Fig. 69) containing finely divided iron as a catalyzer, a few per cent of the gases combine.

$$N_2+3H_2\rightleftarrows 2NH_3+24{,}000 \text{ cals.}$$

The ammonia is dissolved to form ammonium hydroxide solution, and drained away at *B*; while the uncombined nitrogen and hydrogen are pumped back and reintroduced into the reaction chamber. This is the **direct synthesis of ammonia** (sometimes called the **Haber process**). The hydrogen it consumes usually comes from water gas (§ 69).

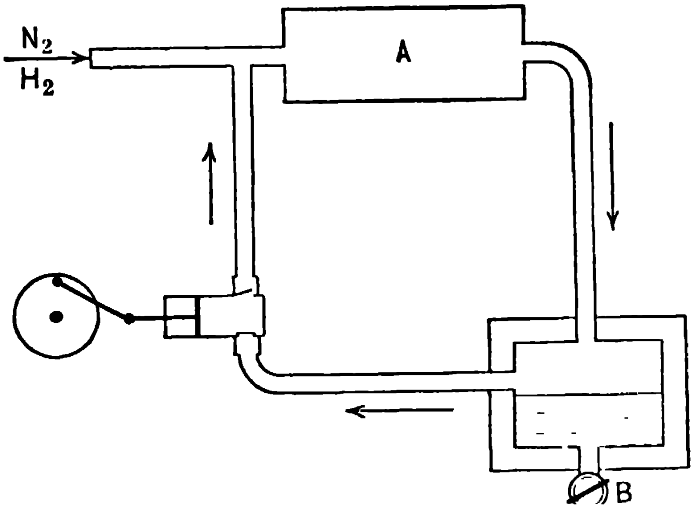


Fig. 69—Sketch to illustrate the principle of the direct synthesis of ammonia (Haber process)

A mixture of gases, containing nitrogen and hydrogen in proper proportions for the preparation of ammonia by direct synthesis, may in fact be prepared by passing a mixture of steam and air over white-hot coke Carbon monoxide, produced at the same time, may be largely removed by oxidation with steam, in the presence of a catalyzer:

$$CO+H_2O \rightleftarrows CO_2+H_2;$$

while the carbon dioxide, if the mixture of gases is compressed, dissolves readily in water (Henry's Law, § 128).

2. **The Cyanamide Process.** A second process for synthesizing ammonia proceeds indirectly, in three steps.

(*a*) Limestone is reduced by coke in an electric furnace, giving calcium carbide, CaC_2 (§ 457).

(*b*) The carbide is then heated to a white heat (about 1000° C.) and nitrogen (from liquid air) passed over it:

$$CaC_2+N_2=CaNCN+C.$$

The product is **calcium cyanamide, CaNCN**—not the same thing as calcium cyanide, $Ca(CN)_2$.

(*c*) The final step is the decomposition of the cyanamide in closed autoclaves, by high-pressure steam:

$$CaNCN+3H_2O=CaCO_3+2NH_3.$$

The cyanamide process appears to have an economic advantage over the Haber process, and was extensively developed by all the principal belligerents, during the Great War. Germany is believed to have had an annual production of about 600,000 tons of ammonia by this process at the time of the Armistice. The largest of the several American plants was at Muscle Shoals, Alabama.

285. Preparation of Ammonia in the Laboratory.—When a cylinder of liquefied ammonia is not available, the gas may be generated in the laboratory:

(1) **By heating a concentrated solution of ammonium hydroxide.**

$$NH_4OH = H_2O + NH_3 \uparrow .$$

(2) **By heating a solution of an ammonium salt with an active base:**

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O + 2NH_3 \uparrow .$$

In either case the gas must be dried by passing through a cylinder filled with quicklime (*B*, Fig. 70).

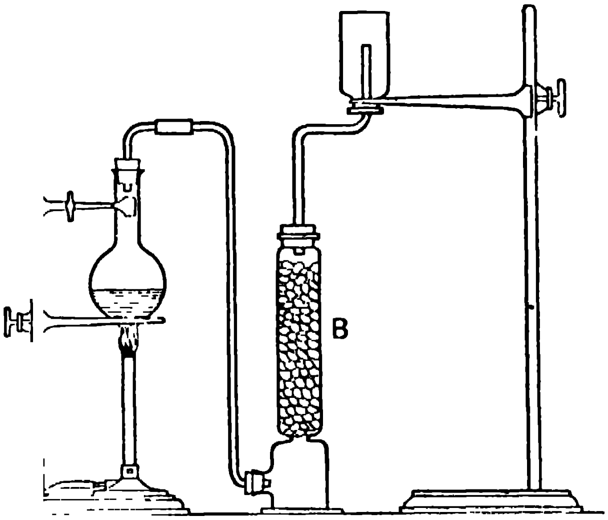


Fig. 70.—Preparation of ammonia in the laboratory.

Notice that *ammonia cannot be prepared merely by heating an ammonium salt.* Such salts are partly dissociated (§ 131), to be sure, when strongly heated:

$$NH_4Cl \rightleftarrows NH_3 + HCl;$$

but a large part of the ammonium chloride sublimes (§ 196) and recondenses in the colder parts of the apparatus, undecomposed. Furthermore, the *products of the reaction, NH_3 and HCl, are both volatile, pass off together, and recombine at the first opportunity.* By diffusion through a porous plug these products could be partially separated.

Ammonium sulfate would give no better result, since even sulfuric acid is volatile at the temperature necessary to decompose the salt. Phosphoric acid is non-volatile, and ammonium phosphate, unlike other ammonium salts, is therefore completely and irreversibly dissociated on heating.

To test for ammonium salts, heat a little of the material in a test-tube with a solution of sodium hydroxide. Ammonia gas will be expelled, and may be recognized by its odor or by its action on moist red litmus.

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3 \uparrow .$$

Write this equation in ionic form.

286. Physical Properties of Ammonia.— 1. Ammonia is **extremely soluble** in water (demonstrated as with HCl, Fig. 49, § 178). One volume of water will absorb about 800 volumes of ammonia at ordinary temperatures. The solution increases in volume during the process of absorption— so much that it may have a specific gravity as low as 0.90.

Note, however, that this is not a case of simple solution, for a part of the ammonia combines with the water, to form **ammonium hydroxide:**

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

2. Ammonia is **easily condensed to a colorless liquid** (a pressure of 8.5 atmospheres is sufficient, at 20° C). Liquid ammonia comes on the market in steel cylinders, chiefly for use in refrigeration. It is an **important solvent,** dissolving such utterly diverse things as inorganic salts, sulfur, iodine, organic resins, and even metallic sodium. Chemists are interested in the fact that it is an ionizing solvent, furnishing conducting solutions of acids, bases, and salts (§ 252).

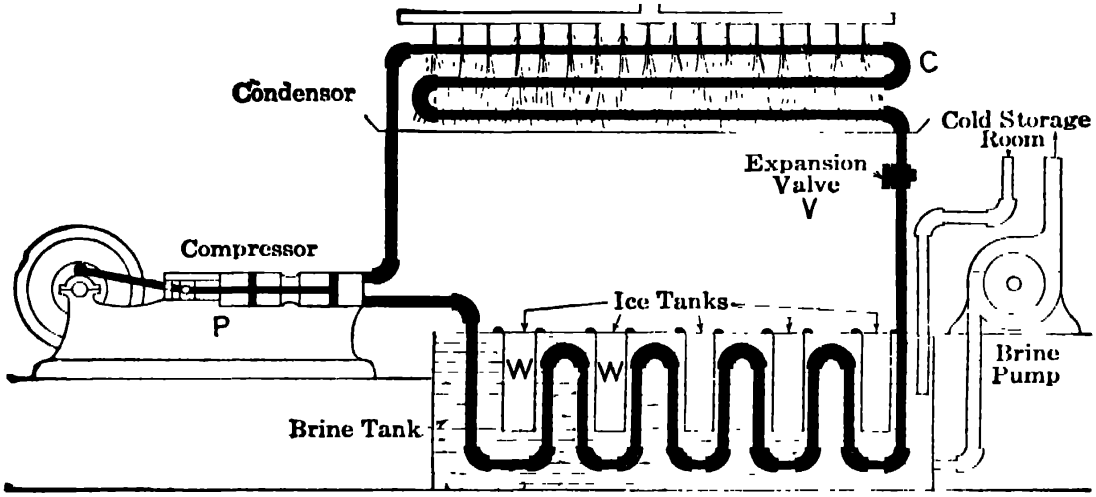


FIG. 71.—Diagram of ice plant using ammonia.

287. Ammonia in Refrigeration.— The principal uses of ammonia are (1) refrigeration and manufacture of ice; (2) manufacture of soda by the Solvay process (§ 437); (3) manufacture of nitric acid by catalytic oxidation (§ 298).

Fig. 71 shows the essential features of a plant for refrigeration and manufacture of ice. Ammonia gas is liquefied by a compression pump at *P*, thence passes through a set of coils, *C*, cooled by a spray of cold water, to remove the heat liberated in liquefaction. On passing through an expansion valve, *V*, the pressure is suddenly decreased, and the liquid evaporates, experiencing a fall in temperature because of the energy expended in evaporation. The low-pressure pipe, carrying the expanded and cooled ammonia, returns by way of a brine tank, to the pump where the gas is recondensed.

The brine in the brine tank is cooled by the circulating ammonia to perhaps 10° below the freezing point of water; thence it circulates around tanks of distilled water, *W*, which freeze into solid cakes of ice. The return of the brine to the brine tank is by way of refrigerator rooms. Without cold storage, the provisioning of our large cities during the summer months would be almost impossible. Modern refrigerator rooms are of very large size and are regulated by thermostats, the year round, to within a few tenths of a degree of some definite temperature, according to the nature of the material in storage.

288. Chemical Properties of Ammonia.—1. Ammonia **unites directly with acids to form ammonium salts.** (Recall the white cloud that it forms with hydrogen chloride gas or any other volatile acid.)

FIG 72 —A refrigerator room.

Solutions of salts formed by the combination of ammonia with active acids are perceptibly acid toward some indicators (not toward litmus). What does this indicate? Give a detailed ionic formulation.

2. Ammonia is **readily decomposed by heat,** though the decomposition is incomplete at temperatures of 200° or 300°:

$$2NH_3 \rightleftarrows N_2+3H_2.$$

From the fact that the decomposition is rendered more complete by an increase of temperature, do you conclude that it is accompanied by an absorption or an evolution of heat? State the principle involved.

3. Ammonia is **readily oxidized,** especially at high temperatures. In other words, under such conditions it is a **reducing agent.**

(*a*) It will not burn in air; but it will burn in oxygen, with a bright yellow flame (Fig. 73).

(*b*) When passed over heated copper oxide, it is oxidized to nitrogen and water, while the copper oxide is reduced to metallic copper.

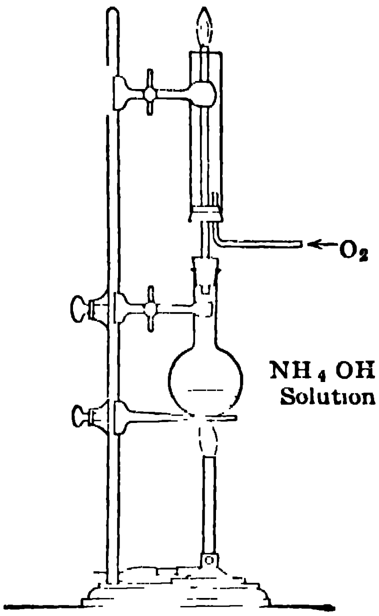


FIG. 73.

(*c*) Chlorine and bromine oxidize ammonia to nitrogen, the halogen in each case being reduced to a hydrohalogen acid:

$$2NH_3+3Cl_2=N_2+6HCl.$$

Why is this regarded as oxidation? Tell what transfer of electrons takes place.

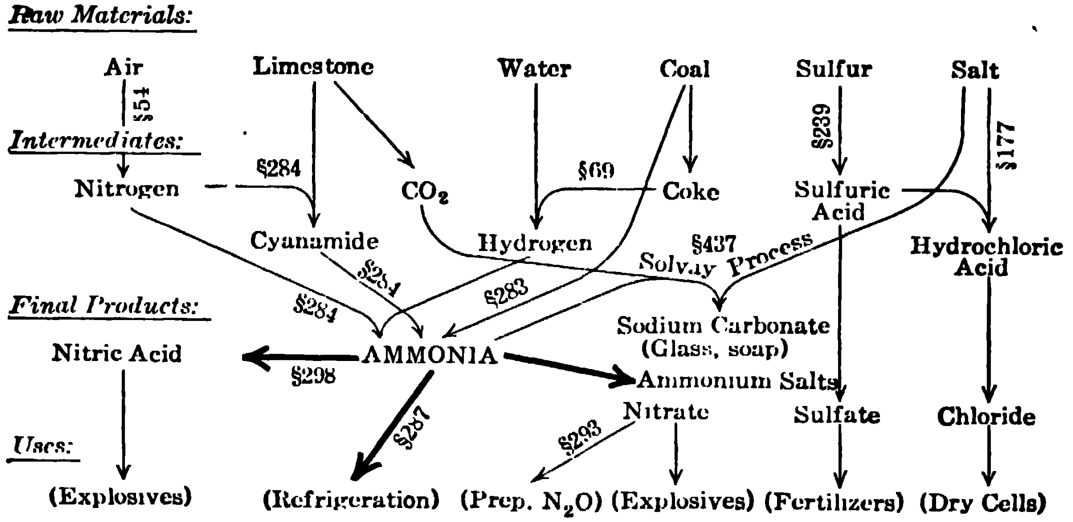
But when ammonia is treated with an excess of chlorine an oily liquid, nitrogen trichloride, NCl_3, is formed. This is a dangerous explosive. Nitrogen iodide, $NI_3 \cdot NH_3$, is a black compound, formed by pouring ammonium hydroxide over iodine crystals. *When dry, this also explodes violently at the slightest touch.*

(*d*) In the presence of an excess of air, with platinum as a catalytic agent, ammonia may be oxidized to *nitric acid* (an important industrial process, § 298).

289. Ammonium Salts.—**Ammonium sulfate** is the source of other ammonium salts, and is used as a fertilizer. **Ammonium chloride** (sal ammoniac) is used in dry cells (§ 125)—more than ten million cells a year in the United States alone. It is also commonly applied to metal surfaces in soldering. Its usefulness for this purpose depends on its partial dissociation by heat into ammonia and hydrochloric acid, which clean the metallic surfaces to which the solder is to be applied by reducing or dissolving oxide that may be present. **Ammonium nitrate,** mixed with one-fourth its own weight of T.N.T. (§ 304) to serve as a detonator, is a powerful explosive. Sawdust, impregnated with ammonium nitrate, has recently been used as a substitute for dynamite.

290. Hydrazine and Hydroxylamine.—Hydrazine, N_2H_4 (colorless liquid) and hydroxylamine, NH_2OH (white solid) are a pair of interesting compounds, representing intermediate stages of reduction between nitrogen itself and ammonia. *Their chemical properties are, in general, like those of ammonia.* Thus, they both unite directly with acids to form salts, but are both decidedly more active bases than ammonium hydroxide; while hydrazine hydrate, $N_2H_4 \cdot H_2O$ is a base, like ammonium hydroxide, $NH_3 \cdot H_2O$, but more stable, and is deprived of water with difficulty. Ammonia acts as a reducing agent only at high temperatures; but hydrazine, even in solution, is one of the most powerful reducing agents known. Hydroxylamine acts similarly, though less energetically.

291. Graphical Summary.


The Industrial Chemistry of Ammonia

The chemical reactions of ammonia are summarized in sec. 306.

EXERCISES

1. What is the commercial source of nitrogen? What impurities would you expect to find in a cylinder of compressed nitrogen?

2. What volume of nitrogen gas may be prepared from 100 cc. of a solution of sodium nitrite, 20 per cent strong, of specific gravity 1.20, by interaction with ammonium chloride?

3. A cylinder of 3 cu. ft. capacity holds compressed nitrogen under a pressure of 50 atmospheres. Estimate the weight of the gas, in pounds (§ 147).

4. Which is the cheaper fertilizer per pound of nitrogen, ammonium sulfate, at $70 a ton, or sodium nitrate of the same purity, at $60 a ton?

5. Calculate the weight of a liter of dry nitrogen gas, at 20° C., and 740 mm. pressure.

6. What two elements of the atmosphere combine with magnesium, when this metal is burned in air? Write equations to show what happens when the two compounds thus formed are dissolved in water.

7. In the cyanamide process, what would you presume the products to be, if air, rather than nitrogen, were passed over calcium carbide, at a white heat?

8. When electric sparks are passed through a mixture of nitrogen and hydrogen contained in a glass tube, very little combination occurs. But if a few drops of concentrated sulfuric acid are placed in the tube, the reaction goes on to completion. The effect is not due to increased electrical conductivity in the presence of sulfuric acid, nor is it a case of catalysis. What is your best explanation?

9. Write balanced equations for the preparation of ammonium sulfate,

carbonate, sulfite, and acid sulfite, from ammonia, water, and an acid anhydride.

10. Ammonium chloride cannot be prepared by treating ammonium sulfate with hydrochloric acid. But if a solution of ammonium sulfate is treated with a solution of barium chloride the reaction is complete. Explain.

11. With ammonium sulfate at $70 a ton and slaked lime at $10 a ton, calculate the cost of the materials needed for a ton of liquid ammonia, assuming a 90 per cent yield (§ 191).

12. Write and balance equations for:
(*a*) Action of slaked lime on sodium acetate;
(*b*) Action of caustic soda on sal ammoniac;
(*c*) Preparation of ammonium fluoride from ammonia;
(*d*) Hydrolysis of calcium cyanamide;
(*e*) Burning ammonia gas in oxygen.

13. Samples of four white salts are known to be NH_4Cl, $(NH_4)_2SO_4$, $NaCl$, and Na_2SO_4. Tell how each may be identified and distinguished from the others.

14. Explain why ammonia can be prepared by heating ammonium phosphate alone, whereas ammonium chloride needs to be mixed with slaked lime or some similar substance.

15. Explain why ammonium sulfate cannot be transformed into ammonium acetate by distillation with acetic acid. Tell how you might effect the transformation, in two steps, proceeding by way of gaseous ammonia. Write equations.

16. Which of the following substances could be used to dry ammonia gas? Which could not, and why: H_2SO_4, $CaCl_2$, CaO, Na?

17. What volume of ammonia gas is needed to reduce 1 g. of cupric oxide to metal?

18. With aid of the index, prepare a list of the catalyzers that have been mentioned in this and previous chapters of the text, with their uses.

19. Concentrated ammonium hydroxide solution has a specific gravity of 0.88 and contains 35 per cent NH_3. What volume of this reagent corresponds to a kilogram of commercial (95 per cent) ammonium sulfate?

20. Find three different ways, direct or indirect, for proving that ammonia contains hydrogen.

21. Give an equation for the action of bromine on ammonia, forming nitrogen and hydrogen bromide. Why is this considered as a case of oxidation and reduction?

CHAPTER XXII

NITRIC ACID AND RELATED COMPOUNDS

292. The Oxides of Nitrogen.—Nitrogen unites with oxygen in five different stages; but only the three listed here in black type are of importance:

Name.	Formula	Color.	Action on Water.
Nitrous oxide	N_2O	Colorless gas	Fairly soluble
Nitric oxide	NO	Colorless gas	Slightly soluble
Nitrogen trioxide	N_2O_3	Blue liquid (−21°)	Gives HNO_2
Nitrogen tetroxide (peroxide)	$N_2O_4 \rightleftarrows 2NO_2$	Yellow to brown gas	Gives HNO_3 and NO
Nitrogen pentoxide	N_2O_5	White solid	Gives HNO_3

293. Nitrous Oxide.—Nitrous oxide, N_2O, is **a colorless gas, formed by gently heating ammonium *nitrate*.** Too rapid heating may result in a **violent explosion.**

$$NH_4NO_3 = 2H_2O + N_2O \uparrow .$$

Compare with the heating of ammonium *nitrite* (§ 281).

Nitrous oxide will support combustion of phosphorus, carbon, and many other elements, and will even cause a glowing splint to burst into flame, after the fashion of oxygen. Like Cl_2, NH_3, CO_2, and SO_2, it is easily condensed by pressure, and is sold in liquid form , in steel cylinders. It is used for anesthesia, in dentistry and surgery, in admixture with oxygen.

294. Nitric Oxide.—Nitric oxide, NO, is formed **whenever nitrogen and oxygen are heated together to the temperature of the electric arc** (around 3000° C.). **It is itself colorless, but unites with extra oxygen, whenever it comes in contact with air, to form a brown gas, nitrogen peroxide, NO_2.**

The formation of nitric oxide and nitrogen peroxide may readily be demonstrated in the lecture-room by sending sparks, from a powerful induction coil, between platinum terminals in a glass globe filled with air. Presently the brown color of nitrogen peroxide appears. If a few drops of water are then added, this gas dissolves, forming an acid solution (HNO_3). This experiment illustrates a method (§ 299) by which thousands of tons of nitric acid are now manufactured each year from the atmosphere.

The common **laboratory method** for preparing nitric oxide is **by reducing somewhat diluted nitric acid with copper.**

The equation for this reaction (balanced in § 133) is often written in molecular form:

$$3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O.$$

But this tends to disguise the fact that the essential change is here a transfer of electrons. Write an ionic formulation of this reaction (§ 276) and explain what transfer of electrons take place.

295. Nitrogen Peroxide.—(1) Nitrogen peroxide, the brown gas produced when nitric oxide unites with oxygen, differs from the two other gaseous oxides of nitrogen **in dissolving readily in water.** This is really a chemical combination, the products being nitric acid and nitrous acid:

$$2NO_2+H_2O \rightarrow HNO_3+HNO_2.$$

(2) At ordinary temperatures, nitrogen peroxide has almost twice the density that corresponds to its formula, NO_2, and a color which is more yellow than brown. This is due to the formation of nitrogen tetroxide, N_2O_4, by combination of two molecules of NO_2.

We have here a case of association (§ 157). Pure N_2O_4 is colorless; but as the temperature is raised it dissociates more and more into NO_2, passing through yellow and light brown to a deep chocolate brown (around 150° C.). At still higher temperatures the color fades away again, on account of dissociation of NO_2 into NO and O_2. On cooling, the same changes occur in reverse order:

$$\underset{\text{Colorless}}{N_2O_4} \rightleftarrows \underset{\substack{\text{Brown}\\150^\circ}}{2NO_2} \rightleftarrows \underset{\substack{\text{Colorless}\\600^\circ}}{2NO+O_2}.$$

The yellowish-brown gas at room temperature is about half N_2O_4 (by volume). (Calculate the weight of a liter of it at standard conditions on this assumption).

(3) **Nitrogen peroxide is poisonous.** It is a **good oxidizing agent,** and its most important use, in the manufacture of sulfuric acid (§ 240) depends upon this property. It is sometimes employed in traces, for bleaching flour.

296. Nitrous Acid and Nitrites.—When equal volumes of NO and NO_2 are passed into water, we get a solution which is assumed to contain **nitrous acid,** HNO_2:

$$NO+NO_2+H_2O \rightleftarrows 2HNO_2.$$

Nitrous acid, like carbonic acid, H_2CO_3, and sulfurous acid, H_2SO_3, has never been prepared pure, but is assumed to exist because solutions prepared as just described are acid toward litmus, and when neutralized with bases and evaporated, yield salts, such as sodium nitrite, $NaNO_2$.

Nitrous acid solutions, prepared from NO and NO_2, or by acidifying a solution of a nitrite, are extremely *unstable*, decomposing slowly at room temperatures, liberating NO and NO_2. Thus nitrous acid, like NO_2 itself, is an *oxidizing agent.*

Sodium nitrite may be prepared (1) by passing NO and NO_2 into NaOH solutions; (2) by heating sodium nitrate for a long time above its melting point; or (3) by melting sodium nitrate with metallic lead. (In the latter case the lead is oxidized to litharge, PbO). Sodium nitrite is an important reagent, used in large quantities in the manufacture of dyes (§ 372). The United States is estimated to consume about 4000 tons of this salt each year (1920).

297. Nitric Acid from Nitrates.—Review 105. Nitric acid is prepared commercially by distilling sodium nitrate with concentrated sulfuric acid. The retort (*R*, Fig. 74) is a cast-iron vessel holding several tons. Any portion of the vapors that escape being condensed in the water-cooled condenser (*C*) are forced to pass upward through a tower of stoneware, and are there dissolved by a spray of water, to form dilute nitric acid.

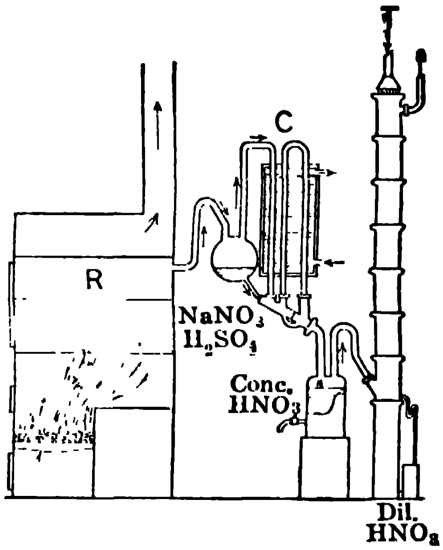


Fig. 74—Commercial preparation of nitric acid from sodium nitrate.

298. Nitric Acid from Ammonia.—Nitric acid has recently been prepared on a large scale by passing ammonia gas, with an excess of air, over a catalyzer consisting of rolls of platinum gauze.

The temperature is held around 750°, at first by electrical heating; but when the reaction is well started it liberates enough heat to maintain the catalyzer at the proper temperature, provided the incoming gases are in the correct proportion. At the time of the Armistice, in 1918, the United States was able to produce 200,000 tons of nitric acid a year by this method.

Review § 229. Explain why a catalyzer is necessary in oxidizing ammonia to nitric acid.

299. Nitric Acid from the Atmosphere.—Thousands of tons of nitric acid are now produced each year, with the aid of the electric furnace, from the nitrogen and oxygen of the atmosphere, chiefly in Norway and Switzerland.

$$N_2+O_2 \rightleftarrows 2NO(3000^\circ \text{ C.})$$

$$2NO+O_2 \rightleftarrows 2NO_2 \ (400^\circ \text{ C., and below}).$$

$$3NO_2+H_2O=2HNO_3+NO \ (40^\circ \text{ C.}).$$

Since the formation of NO (first reaction) absorbs heat, it is most complete at high temperatures (§ 219). At somewhat lower temperatures the reverse reaction predominates, and NO once formed, tends to dissociate again into N_2 and O_2. Accordingly **the mixture of gases leaving the electric furnace must be cooled, as suddenly as possible,** to temperatures so low (400° C.) that the reverse reaction becomes reasonably slow. The NO then combines with more oxygen to form NO_2, which is dissolved in water to form HNO_3.

The furnace designed by Birkeland and Eyde is shaped somewhat like a huge cheese, 8 ft. in diameter, and 2 ft. thick. There is a flattened cavity in the center, into which project two hollow, water-cooled, copper electrodes. Fig. 75 shows the apparatus cut through in the middle, with the right half removed, in order to expose the flat cavity which contains the electrodes, and in which the reaction takes place. A large electromagnet, one-half of which is here shown, has the effect of spreading out the electric arc into a flat disc, which fills the whole interior of the reaction-chamber.

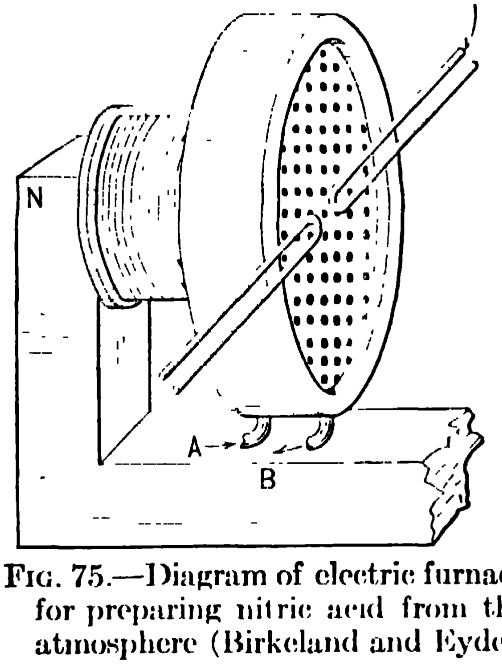


FIG. 75.—Diagram of electric furnace for preparing nitric acid from the atmosphere (Birkeland and Eyde).

Air enters through a passageway at *A*; streams out into the disc of flame, through the numerous small openings shown in the figure; then passes downward and out, at *B*, mixed with air which has entered in the same way through the other half of the furnace. By this means the mixture of oxygen and nitrogen is exposed momentarily to a temperature of about 3000°, bringing the two into partial combination to form nitric oxide, NO. The gases leaving the furnace are at about 3000° C., and contain about 2 per cent of NO. They are immediately cooled by impinging against a water-cooled metallic surface, in a water-tube boiler. When the temperature has thus been lowered, the nitric oxide combines with a further quantity of oxygen, forming nitrogen peroxide, NO_2. This is afterward further cooled and absorbed in water, forming nitric acid.

300. Physical Properties of Nitric Acid.—Pure nitric acid is a **colorless liquid,** but samples that approach 100 per cent concentration (*fuming nitric acid*) slowly decompose on standing, liberating NO_2 ,which dissolves and colors the liquid yellow:

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

Ordinary "concentrated" HNO_3 (sp. gr. 1.42) contains only about 70 per cent HNO_3 by weight. It is more stable than the fuming acid, and remains almost colorless for a very long time.

301. Chemical Properties of Nitric Acid.—1. Nitric acid, like other acids, **reacts with bases to form salts and water.**

2. Nitric acid is an important **oxidizing agent.**

(*a*) Thus, glowing charcoal will continue to glow when thrust under the surface of the concentrated acid—**a dangerous experiment;** and a plug of wool, in the mouth of a test-tube in which concentrated nitric acid is warmed, is usually set on fire.

(*b*) Hydrogen sulfide is oxidized by dilute nitric acid to sulfur and water (§ 231); and by warm, fairly concentrated nitric acid to sulfuric acid.

Give balanced molecular equations, assuming the dilute acid to be reduced to nitric oxide, and the concentrated acid to nitrogen peroxide. Write the same equations in ionic form.

(*c*) Hydrochloric acid is oxidized to chlorine and water.

$$HNO_3 + HCl \rightleftarrows H_2O + NO + Cl_2.$$

The NO and the Cl_2 combine in part to form an unstable compound, NOCl.

Balance this equation (§ 135). Explain it as a transfer of electrons.

The mixture of concentrated nitric and hydrochloric acids is called **aqua regia.** Gold and platinum, which are so far below hydrogen in the electrochemical series of § 72 that they are not dissolved by dilute non-oxidizing acids, nevertheless unite directly with the free chlorine that is present in aqua regia, forming $AuCl_3$ and $PtCl_4$.

(*d*) Metals are oxidized and dissolved (next section).

302. Stages in the Reduction of Nitric Acid.—When a metal reacts with a non-oxidizing acid, electrons lost by metallic atoms are transferred to hydrogen ions. (Review first part of § 276.) But when a metal reacts with nitric acid, hydrogen is rarely evolved; for the nitrate-ion accepts electrons more readily than does hydrogen-ion, and is thereby reduced (§ 134):

Reduction

Substance	N_2O_5 HNO_3 Nitrates	NO_2	N_2O_3 HNO_2 Nitrites	NO	N_2O	N_2	NH_2OH	N_2H_4 § 290	NH_3
Valence of nitrogen	+5	+4	+3	+2	+1	0			−3

1. If the nitric acid is quite concentrated, each nitrate ion accepts one electron, the valence of nitrogen is lowered from +5 to +4, and the product is NO_2:

$$NO_3^- + 2H^+ + e = NO_2 + H_2O.$$

For the special case in which metallic copper is the reducing agent, each copper atom loses two electrons, producing a copper ion, Cu^{++}, and the complete equation is:

$$2NO_3^- + 4H^+ + Cu = 2NO_2 + 2H_2O + Cu^{++}.$$

What salt of copper can be obtained by evaporating the solution? Write and balance the *molecular equation* (§ 276).

2. If the nitric acid is much diluted, each nitrate ion accepts three electrons, the valence of nitrogen is lowered from +5 to +2, and the product is NO:

$$NO_3^- + 4H^+ + 3e = NO + 2H_2O.$$

Write a complete ionic equation for the special case in which hydrogen sulfide is the reducing agent, the sulfur atom of the H_2S molecule losing two electrons, to form elementary sulfur.

Write equation for the special case in which the reducing agent is metallic copper.

3. If the nitric acid is very dilute, or if the reducing agent is very active (a metal toward the top of the electrochemical series), each nitrate ion may accept as many as eight electrons. Thus the valence of nitrogen is lowered from +5 to −3, and the product is ammonia gas, or an ammonium salt:

$$NO_3^- + 10H^+ + 8e = NH_4^+ + 3H_2O.$$

If the nitric acid is to be completely reduced, some other active acid (H_2SO_4) must be present to supply the necessary concentration of hydrogen-ion.

Write an ionic equation for the complete reduction of a small amount of nitric acid by metallic iron, each iron atom losing two electrons. What ferrous salt and what ammonium salt can be obtained on evaporating the solution? Write and balance the corresponding molecular equation.

Note that in every case **the reduction of nitric acid calls for hydrogen ions, as well as electrons, and produces water.**

But since $H^+ + e = H$, we might think of the reduction as being accomplished by *nascent hydrogen*: namely by hydrogen existing for the moment as individual atoms, rather than as molecules. This assumption is, however, not well supported by experimental evidence, and is going out of favor.

Write unbalanced ionic formulations for the oxidation of phosphorus to phosphoric acid, and iodine to iodic acid, by concentrated nitric acid.

Balance these formulations, first adjusting the atoms that change valence, then oxygen, and finally hydrogen. Check by counting charges on ions.

Write and balance an ionic equation for the reduction of dilute nitric acid to nitrous oxide by metallic zinc. Another for the reduction of a very dilute nitric acid solution, in the presence of an excess of sulfuric acid, by metallic aluminum, forming an ammonium salt. Write the molecular equation for this reaction.

303. Tests for Nitrites and Nitrates.—Nitrites and nitrates are both easily reduced to nitric oxide (NO) by adding an excess of an acid solution of a ferrous salt (i.e., ferrous-ion):

$$\underset{\text{Nitrite-ion}}{NO_2^-} + Fe^{++} + 2H^+ = Fe^{+++} + NO + H_2O$$

$$\underset{\text{Nitrate-ion}}{NO_3^-} + 3Fe^{++} + 4H^+ = 3Fe^{+++} + NO + 2H_2O$$

The NO thus produced unites with the excess of ferrous ion, producing a dark-brown color, presumed to be due to the complex-ion, $Fe \cdot NO^{++}$. The first of these two reactions takes place readily, even in a very faintly acid solution, while the second requires the solution to be rather strongly acid (i.e., a large excess of hydrogen-ion). Accordingly, ***nitrites* are distinguished from *nitrates* by the fact that they develop a brown color with an excess of a ferrous salt, even in a solution which is only faintly acid with acetic acid;** while nitrates give this test only when an active acid, such as sulfuric acid, is present.

What acids do you think might be substituted for acetic acid in this test, and why? Formulate the two reactions given above, in terms of molecules.

304. Uses of Nitrates and Nitric Acid.—The United States, in normal times, consumes about half a million tons of sodium nitrate each year, as *fertilizer*. In addition, about 100,000 tons of concentrated nitric acid are used annually, chiefly in the production of **dyes, cinematograph films, lacquers, rayon** (§ 370), **celluloid, and a great many important explosives**: nitroglycerol, smokeless powder, dynamite, trinitro-toluene (T. N. T.), and others.

305. Cycle of Nitrogen in Nature.—1. Careful experiments have shown that all the nitrogen required for the growth of the higher plants is absorbed through their roots, as *nitrogen compounds* -- chiefly nitrates. The nitrogen of the atmosphere is of no use, as long as it remains in the elementary condition. Uncombined, nitrogen is a mere restrainer of the activity of oxygen; combined, it is plant food.

There are several processes in nature that *fix* nitrogen, or *bring it into combination with other elements*. Every lightning flash causes a little of the nitrogen of the atmosphere to unite with oxygen, to form nitric oxide (§ 294). This dissolves in water to form nitric acid, which reacts with the limestone of the soil to form calcium nitrate.

The amount of nitrogen thus fixed in any one year is very slight—a few ounces, at most, over each acre of the earth's surface. But nature may, on occasion, take a million years for her work; and it seems possible that the thunderstorms of the ages that preceded the appearance of life upon the earth had much to do with making that life possible. Man now duplicates the work of the lighting in electric furnaces (§ 299), producing either nitric acid, to be used in the manufacture of explosives, or calcium nitrate, to be sold as fertilizer.

2. Although the higher plants are seemingly quite unable to make use of the nitrogen of the atmosphere, many bacteria do so readily. These are the **nitrogen-fixing bacteria,** the most famous of which are those that produce the abnormal swellings or nodules on the roots of certain leguminous plants (cow-peas, clover, and alfalfa). These bacteria are foreign invaders of the root tissue, and the plant makes a desperate effort to drive them out. But if they succeed in maintaining their foothold, and the disease becomes incurable, it turns out to be a blessing; for the nitrogen that is fixed by the bacteria is handed on, in the combined form, to the plant that serves as their host. Clover always grows much more luxuriantly when nitrogen-fixing bacteria are present.

Nitrogen, once fixed by the two processes we have described, tends to run through a definite **cycle,** which is outlined by the diagram on the next page.

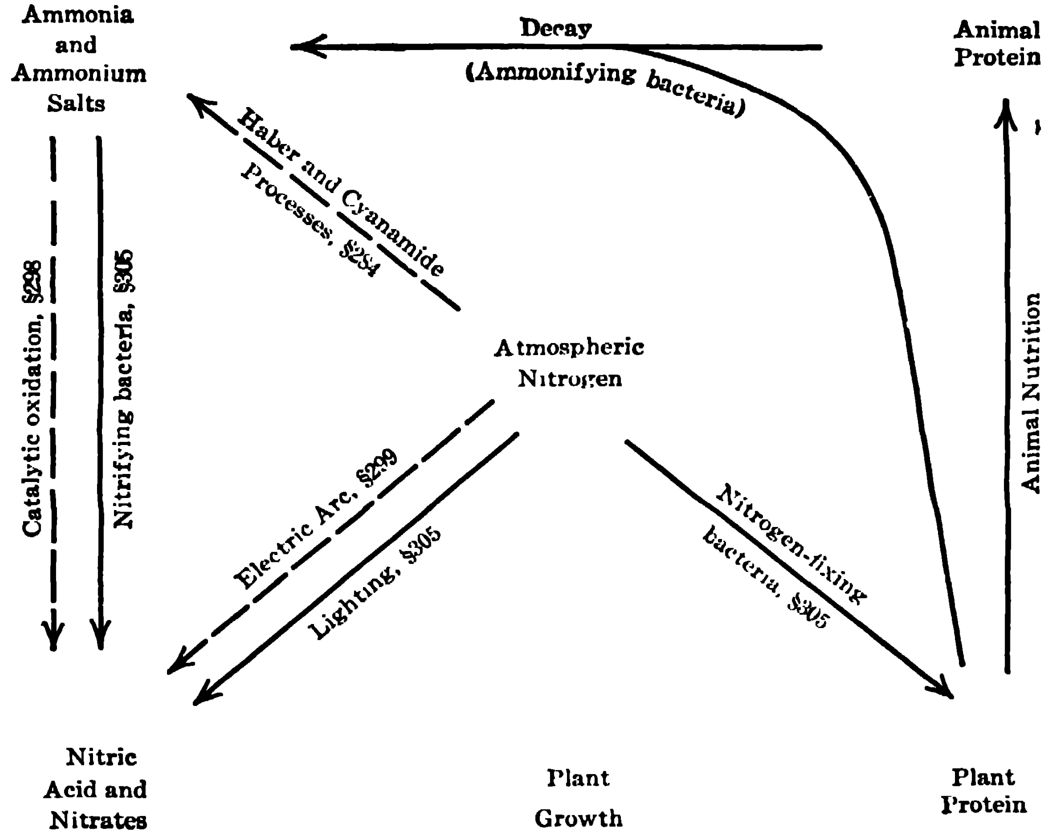
3. Nitrogen compounds, absorbed through the rootlets of growing plants, are transformed into *plant protein,* which serves as food for animals, and becomes *animal protein.*

4. When plants and animals decay, their nitrogen is converted into ammonia or ammonium salts by the **ammonifying bacteria.**

5. Ammonium salts are not readily absorbed by most plants. The fact that we can use them (or even calcium cyanamide, § 284) as fertilizers, is due to the fact that most soils contain **nitrifying bacteria,** which convert them into a more acceptable plant food. A growing corn-plant may be made to absorb so much sodium nitrate that crystals of that salt may be shaken from the dried split stalk.

The cycle of nitrogen is thus repeated endlessly, and every atom of nitrogen in our own bodies may have passed through plants and animals, not once, but many times. Were this cycle broken, life upon the earth would soon cease. Some of the most important problems before the chemists of to-day concern the development of new or better ways of fixing nitrogen, or of preventing it, once fixed, from returning again to the atmosphere. Were it not for progress already made (§§ 281, 299) the approaching exhaustion of the nitrate deposits of Chile might have brought the more thickly populated countries of the world into a state of chronic famine before the end of the present century.

306. Graphical Summary.—Full-line arrows show the cycle of nitrogen in nature. Dotted arrows show related industrial processes.


Ammonia and Ammonium Salts
Decay (Ammonifying bacteria)
Animal Protein
Haber and Cyanamide Processes, §284
Catalytic oxidation, §298
Nitrifying bacteria, §305
Animal Nutrition
Atmospheric Nitrogen
Electric Arc, §299
Lightning, §305
Nitrogen-fixing bacteria, §305
Nitric Acid and Nitrates
Plant Growth
Plant Protein

EXERCISES

1. Write equations for the oxidation of each of the following by concentrated nitric acid:

H_2S, Na_2SO_3, ZnS, P, S, C, Sn, Cu, Fe, NaCl.

2. Describe tests by which you would distinguish between two solutions:

(*a*) One containing a nitrate, the other a nitrite;

(*b*) One a nitrate, the other a chlorate;

(*c*) One a sulfate, the other a sulfite;

(*d*) One sodium sulfide, the other sodium hydroxide;

(*e*) One a bromide, the other an iodide;

3. Write equations for all reactions involved in the preceding tests.

4. Explain why HNO_3 can be used to prepare CO_2 from Na_2CO_3, but not to prepare SO_2 from Na_2SO_3. Write equations.

5. How would you determine whether a sample of NO contained N_2O?

6. Give an equation to explain why nitric acid becomes brown on being heated.

7. Apply the principle of Le Chatelier (§ 221) to determine whether the

dissociation of N_2O_4 becomes more or less complete when the pressure on the gas is increased.

8. Assuming a 95 per cent yield, what weight of Chile saltpeter, 90 per cent pure, is needed to prepare a ton of concentrated nitric acid, 68 per cent pure?

9. Write equations for all the reactions to be expected on distilling sodium iodide with dilute nitric acid (§ 192, item 4).

10. State the circumstances that determine the nature of the reduction products to be expected when nitric acid is reduced by a metal. Illustrate with ionic equations.

11. Give equations to show the part played by the oxides of nitrogen in the manufacture of sulfuric acid by the chamber process.

12. Explain why nitric acid will dissolve copper readily in the cold, while hydrochloric acid will not, in spite of the latter being somewhat the more active.

13. State the conditions that determine whether a catalyzer may prove useful in carrying out a given reaction, or whether an increased yield may better be secured by raising the temperature.

14. A liter of normal nitric acid is mixed with 1200 cc. of normal ammonium hydroxide. What will be the normality (as acid or base) of the resulting mixture. The mixed solution is evaporated to dryness. What will be the weight of the residue?

15. Given nitrogen gas, tell how you might convert it successively into: a nitride, ammonia, nitric acid, a nitrate, a nitrite, ammonium nitrite, nitrogen.

16. Give equations for two different commercial methods for preparing synthetic ammonia Assuming a perfect yield, what volume of ammonia is produced by each process from one volume of elementary nitrogen?

CHAPTER XXIII

PHOSPHORUS AND ARSENIC

Toward the end of the seventeenth century, a German alchemist, in his search for the philosopher's stone—a fabled preparation for converting common metals into gold—came, quite by accident, upon a substance having the property of glowing in the dark. This was phosphorus (Greek, *light-bearer*), now consumed in enormous quantities in the preparation of matches, and mined by thousands of shiploads, in the form of calcium phosphate, to be used as fertilizer.

307. Occurrence of Phosphorus in Plants and Animals.—Phosphorus is quite as necessary to life as nitrogen itself. The bony framework and teeth of vertebrates are largely *calcium phosphate.* The brain and nervous tissue of the higher animals contain phospho-proteins (§ 388). Indeed, **a minute amount of phosphorus is contained in each individual cell of every living plant and animal**—in the cell-nucleus, the structural element most intimately associated with the phenomena of growth and reproduction.

308. Phosphorus Minerals.—Phosphorus occurs in nature only as salts of orthophosphoric acid, H_3PO_4. An important mineral of phosphorus is **apatite,** a double salt of the composition $CaF_2 \cdot 3Ca_3(PO_4)_2$—namely, one molecule of calcium fluoride in association with three of calcium phosphate. Frequently the fluorine is partly or wholly replaced by chlorine. Apatite is found in crystalline igneous rocks (§ 395) in all parts of the world, and minute crystals occur in many soils. The most important deposits of the mineral are in Ontario, Canada.

By action of carbonic acid and running water, apatite and other phosphate minerals are brought into solution and become available for growing plants. These, in their turn, hand on the element to animals. Thus, certain important secondary phosphate minerals have been formed in nature—impure forms of calcium phosphate. These are roughly described as *phosphate rock.*

On the ocean bottom in many parts of the world are found *phosphatic nodules,* consisting of calcium phosphate which has been dissolved from the bones and teeth of fish and then redeposited around nuclei of unchanged material.

Limestone beds often contain considerable amounts of calcium phosphate, intermingled with the predominating calcium carbonate. These deposits are often leached by running water after being uplifted into dry land, leaving the phosphatic pebbles or nodules behind, associated with clay.

No other country approaches the United States in richness of phosphate resources. The deposits occur so near the surface as to be mined in open pits, and concentrated by washing away the lighter sand, clay, and gravel with running water. As much as 3,000,000 tons have been mined in a single year, most of which is exported to Central Europe to be used as fertilizer. About three-fourths of the output has come from Florida, but large quantities are mined in South Carolina and Tennessee. In the Northern Rocky Mountain District (Idaho, Utah, and Wyoming) not far from the Yellowstone Park, are deposits said to contain billions of tons, as yet practically untouched.

309. Preparation of Elementary Phosphorus. At the present time, **phosphorus is commonly prepared in electric furnaces, in which calcium phosphate, sand, and powdered coke are heated together at a high temperature:**

$$Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5,$$

$$P_2O_5+5C=5CO+2P\uparrow$$

The sand unites with calcium oxide to form calcium metasilicate, $CaSiO_3$; and the phosphoric anhydride, P_2O_5, thus set free, is immediately reduced by the carbon to elementary phosphorus, which distils away through an opening near the top of the furnace, and is condensed in cold water.

310. Physical Properties of Phosphorus.—Phosphorus, like sulfur and many other elements, exists in several allotropic forms. The two best known are a waxy, white solid (usually yellowish on the surface), and a red powder.

White (yellow) phosphorus is *extremely poisonous*, and so *inflammable* that it will catch fire from the heat generated by its slow oxidation when exposed to the air. It must never be touched with the fingers, and must be preserved and cut up under water.[1]

Red phosphorus is quite variable in its specific gravity and other physical properties; it is presumed to consist of a solid solution (§ 91) of the white form in a black modification (obtainable by heating the white to a high temperature under great pressure). It is the more stable form of phosphorus, and is most conveniently obtained by heating the white (yellow) form with a trace of iodine, which catalyzes the transformation. It is practically **non-poisonous,** insoluble in CS_2 and other solvents for the yellow form, and ignites only when strongly heated. By being distilled, it may be reconverted to the yellow form. Both forms, of course, give the same product when burned in the air.

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[1] Or a saturated solution of copper sulfate, which coats the sticks over with a layer of metallic copper, and makes them safer to handle.

311. Matches.—Most of the elementary phosphorus produced is consumed in the match industry. In former years, yellow phosphorus was used; but workmen suffered so seriously from chronic phosphorus poisoning that such matches were taxed out of existence. At the present time, only red phosphorus and a sulfide of phosphorus, P_4S_3, are used.

In the *safety match*, the material in the head is S or Sb_2S_3, with a little potassium chlorate or potassium dichromate as an oxidizing agent, powdered glass to increase the friction, and some glue to hold the mass together. This mixture is not combustible enough to be ignited easily, unless struck upon a box coated with red phosphorus.

In the "*diamond match*," the head is usually PbO_2, to serve as an oxidizing agent, with a little P_4S_3 and some dextrin or glue.

312. Phosphine and Phosphonium Salts.—The most important compounds of nitrogen can be matched with phosphorus compounds of corresponding formula. Thus, ammonia, NH_3, corresponds to *phosphine*, PH_3, which unites directly with acids to form *phosphonium salts*, such as phosphonium iodide, PH_4I. These, however, are all completely hydrolyzed by water (a fact which shows that phosphonium hydroxide, if it exists, is an extremely inactive base).

Phosphine itself is commonly prepared as in Fig. 76. The flask contains pieces of yellow phosphorus, covered with sodium hydroxide solution. Air is first displaced from the apparatus by a current of coal gas, passed through a tube dipping beneath the surface of the liquid. Then, on boiling the solution, a part of the phosphorus is oxidized to sodium hypophosphite, NaH_2PO_2, and a part reduced to phosphine. (Balance equation.) The bubbles of phosphine, as they enter the air, catch fire and burn to phosphoric acid, forming a series of "smoke rings."

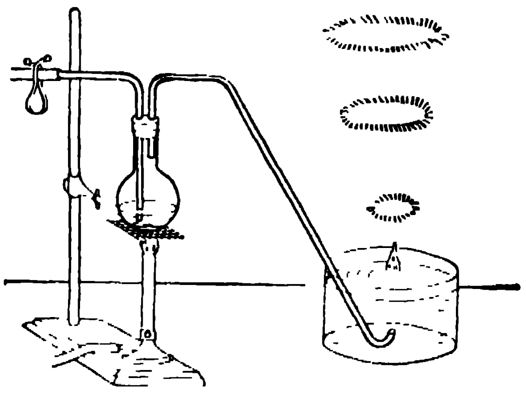


FIG. 76.—Preparation of phosphine.

313. The Three Phosphoric Acids.—In spite of the general correspondence of compounds of the two elements, there are more acids containing phosphorus than there are containing nitrogen;

for N_2O_5 can unite with but one molecule of water, forming $2HNO_3$; while **P_2O_5 can take up water in three distinct stages.**

$$P_2O_5+H_2O=\underset{\text{Metaphosphoric acid}}{2HPO_3}\rightleftarrows 2H^+ + \underset{\text{Metaphosphate ion}}{2PO_3^-},$$

$$P_2O_5+2H_2O=\underset{\text{Pyrophosphoric acid}}{H_4P_2O_7}\rightleftarrows H^+ + (H_3P_2O_7)^- \ \S\,255.$$

$$P_2O_5+3H_2O=\underset{\text{Orthophosphoric acid}}{2H_3PO_4}\rightleftarrows 2H^+ + 2(H_2PO_4)^- \ \S\,255.$$

The three phosphoric acids are all of the same stage of *oxidation* (valence of P, +5) but different stages of hydration.

When we speak of phosphoric acid, without any qualifying prefix, we mean **orthophosphoric acid,** H_3PO_4, which is by far the most important of the acids of phosphorus.

This is formed by oxidizing red phosphorus with concentrated nitric acid (see end of § 302). When orthophosphoric acid is strongly heated, it loses water in two successive stages, giving pyrophosphoric acid, and then metaphosphoric acid. The latter is a glassy, infusible substance, remaining unchanged up to a bright white heat.

Phosphoric acid may be neutralized in three stages (primary, secondary, and tertiary phosphates).

NaH_2PO_4	Na_2HPO_4	Na_3PO_4
$CaH_4(PO_4)_2$	$CaHPO_4$	$Ca_3(PO_4)_2$

314. Superphosphates.—Tricalcium phosphate, or phosphate rock, $Ca_3(PO_4)_2$, has already been mentioned as the principal phosphatic mineral. It is practically insoluble in pure water, and is accordingly but slowly absorbed by growing plants, when spread upon the soil as a fertilizer. Nevertheless, millions of tons of finely ground phosphate rock are used for this purpose, since it is gradually brought into solution by carbonic acid and other slightly active acids present in the soil. A plant with a vigorous and freely branching root-system, such as Indian corn, can make better use of such material than one lacking that advantage.

If ground phosphate rock is treated with a limited amount of sulfuric acid, about half concentrated, it is converted into monocalcium phosphate, $CaH_4(PO_4)_2$, which is soluble:

$$Ca_3(PO_4)_2+2H_2SO_4=CaH_4(PO)_2+2CaSO_4.$$

The **mixture of monocalcium phosphate and calcium sulfate thus produced is called *superphosphate*.** It is one of our most important fertilizers. An excess of sulfuric acid, in the above reaction, would have furnished orthophosphoric acid.

315. Test for Phosphorus.—Small amounts of phosphorus in organic matter are best detected by oxidizing the material with nitric acid, thus securing a solution of orthophosphoric acid. To this is added a solution of ammonium molybdate (a substance of variable formula). There is presently produced a yellow precipitate of **ammonium phosphomolybdate,** $(NH_4)_3PO_4 \cdot 12MoO_3$, namely ammonium phosphate in association with molybdenum trioxide.

316. Arsenic.—Arsenic, the element next below phosphorus in the periodic table, is related to it in much the same way that phosphorus itself is related to nitrogen. It occurs in nature in combination with many metals, as well as with sulfur. **Arsenical pyrites** (mispickel, FeAsS) is the most important mineral. All the soluble arsenic compounds are extremely poisonous (***antidote*, colloidal ferric hydroxide,** § 88).

During the roasting of sulfide ores containing arsenic, the latter is oxidized to As_2O_3, which collects as dust in the flues. From this the element itself may be prepared by reduction with carbon.

Like sulfur and phosphorus, arsenic occurs in several allotropic forms. The most common of these is a crystalline, steel-gray substance, with a bright "metallic" luster. **Chemically, arsenic is definitely a *non-metal*.** Thus it forms no carbonates, nitrates, sulfates, acetates, etc.; and though halogen compounds are known, these—like the phosphorus halides—are completely hydrolyzed in the presence of a large excess of water (§ 191).

317. Arsenic Trioxide and the Arsenites.—Elementary arsenic and its combustible compounds burn in the air to form **arsenic trioxide or arsenious oxide, As_2O_3.** This is a white powder, often called **white arsenic.** It dissolves slightly in water to form a mixture of acids of different degrees of hydration (compare § 313).

$$As_2O_3+H_2O = \underset{\substack{\text{Metarsenious}\\ \text{acid}}}{2HAsO_2} \rightleftarrows H^+ + AsO_2^- \ (\S\ 255),$$

$$As_2O_3+3H_2O = \underset{\substack{\text{Orthoarsenious}\\ \text{acid}}}{H_3AsO_3} \rightleftarrows H^+ + (H_2AsO_3)^- \ (\S\ 255).$$

Arsenic trioxide dissolves much more readily in alkalies than in water, forming solutions of **arsenites.** Concentrated hydrochloric acid dissolves it, forming arsenic trichloride (i.e., arsenious ion):

$$AsO_2^- + 4H^+ = As^{+++} + 2H_2O.$$

Write this in molecular form.

The arsenites are **reducing agents** in alkaline solution, being oxidized to arsenates:

$$AsO_3^{---} + I_2 + H_2O \rightleftarrows AsO_4^{---} + 2H^+ + 2I^+.$$

Since this reaction is reversible, it must be carried out in a faintly alkaline solution, in order that the hydrogen-ion produced may be removed as fast as formed (§ 68). In an acid solution, the reverse reaction takes place; i.e., arsenate-ion acts as an oxidizing agent, oxidizing iodide-ion to elementary iodine.

Rewrite the preceding equation, and restate the comments just made, in terms of molecules instead of ions.

318. Arsenic Pentoxide and the Arsenates.—Arsenic pentoxide, As_2O_5, dissolves in water to form a mixture of three different arsenic acids, corresponding to the three phosphoric acids (§ 313). (Give their names and formulas.) Orthoarsenic acid is obtainable as transparent crystals, which lose water on heating, forming arsenic pentoxide.

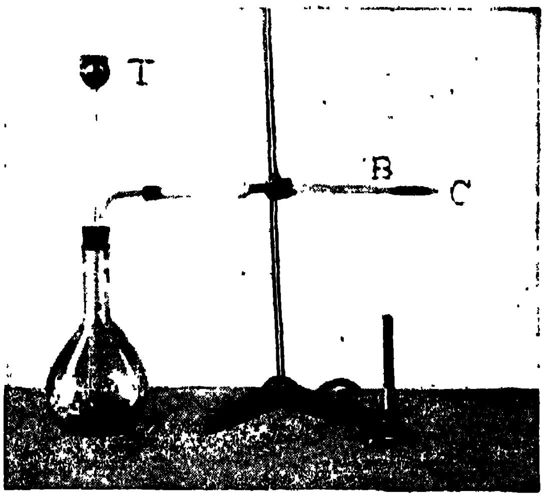


FIG. 77.—The Marsh test for arsenic.

319. Tests for Arsenic.—1. Both arsenites and arsenates give a *yellow precipitate*, consisting largely of arsenic trisulfide, As_2S_3, when hydrogen sulfide is passed into a hot solution, strongly acid with HCl.

2. Arsenates give a *chocolate-brown precipitate* of silver orthoarsenate, with silver nitrate solution. (Give ionic and molecular formulations.)

3. But the most delicate test for arsenic is the *Marsh test*. A hydrogen generator is set up as in Fig. 77, with zinc and hydrochloric acid in the flask. When the air has been completely expelled from the apparatus by the escaping hydrogen (*Be sure!*), the jet is lit at *C*.

On warming the tube at *B*, no dark stain is produced if arsenic is absent from the reagents used. Next, an extract of the material to be tested is poured into the generator through the thistle-tube, *T*. Any arsenic present is immediately reduced to arsine, AsH_3, an extremely poisonous gas, which passes out with the escaping hydrogen, and is burnt at the jet to arsenic trioxide:

$$\underset{\text{Arsenite-ion}}{AsO_2^-}+3Zn+7H^+ \rightarrow AsH_3+3Zn^{++}+2H_2O.$$

If we continue to heat the outlet tube, at *B*, the arsine is there decomposed; and elementary arsenic is deposited a little toward the right, as a brilliant dark brown or black mirror. As little as 0.1 mg. of arsenic can easily be detected by this test. Antimony gives a similar mirror, distinguishable by being non-volatile and insoluble in a solution of sodium hypochlorite.

320. Uses of Arsenic Compounds.—**Arsenic trioxide** is used as an insect poison, and by taxidermists as a preservative for skins. It is an ingredient of some of our best laboratory glassware (pyrex-glass, § 408). An **acid copper arsenite,** $CuHAsO_3$, Scheele's green, is sometimes used as a pigment. Several of our most important insecticides for combating leaf-devouring insects contain arsenic: **Paris green,** which is copper arsenite-acetate, $Cu_3(AsO_3)_2 \cdot Cu(C_2H_3O_2)_2$; **lead arsenate,** $Pb_3(AsO_4)_2$; and solutions of sodium arsenite, mixed with molasses. **Arsenic sulfide** is used for dehairing hides, in the preparation of leather. A number of arsenical organic compounds are now used in medicine.

321. Antimony and Bismuth.—The two elements immediately below arsenic in the periodic table are **antimony** and **bismuth.** These occur in nature both free and as sulfides. Antimony has some non-metallic properties; for salts of metantimonic and pyroantimonic acids are well-known. Bismuth, on the other hand, is exclusively metallic. No true bismuthates are known. **In this, as in other groups of the periodic table, increase in atomic weight causes an increase in metallic properties.**

Both antimony and bismuth, unlike phosphorus and arsenic, form salts in which the element behaves as a metal; sulfates, acetates, carbonates, nitrates, etc. In all of these the metal is *trivalent*. Both antimony and bismuth moreover form salts containing a radical, (SbO) or (BiO), which acts like a univalent metal. These are the *antimonyl* and *bismuthyl* salts (*e.g.*, $K(SbO)C_4H_4O_6$), potassium antimonyl tartrate, or tartar emetic).

All the antimony and bismuth salts are easily hydrolyzed, forming white precipitates (basic salts) of variable composition.

Thus solutions of antimony trichloride and bismuth nitrate, on being poured into water, give precipitates which may, for simplicity, be represented by the approximate formulas, $SbOCl$ and $BiONO_3$, the other product being hydrochloric or nitric acid.

(Write equations in molecular and ionic form.)

Since both of these reactions are reversible, the basic salts concerned may be brought into solution by adding an excess of acid.

On account of hydrolysis it is impossible to have a clear solution of a bismuth or antimony salt, except in the presence of active mineral acids (or certain organic substances, such as tartaric acid).

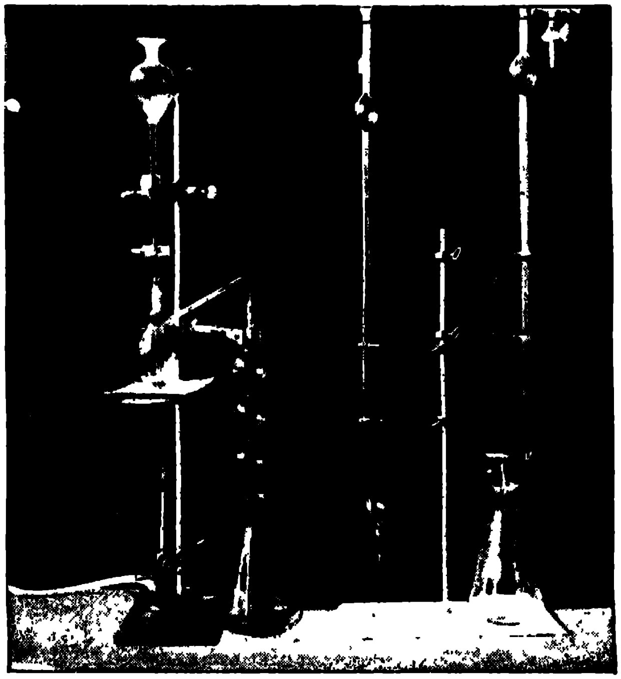


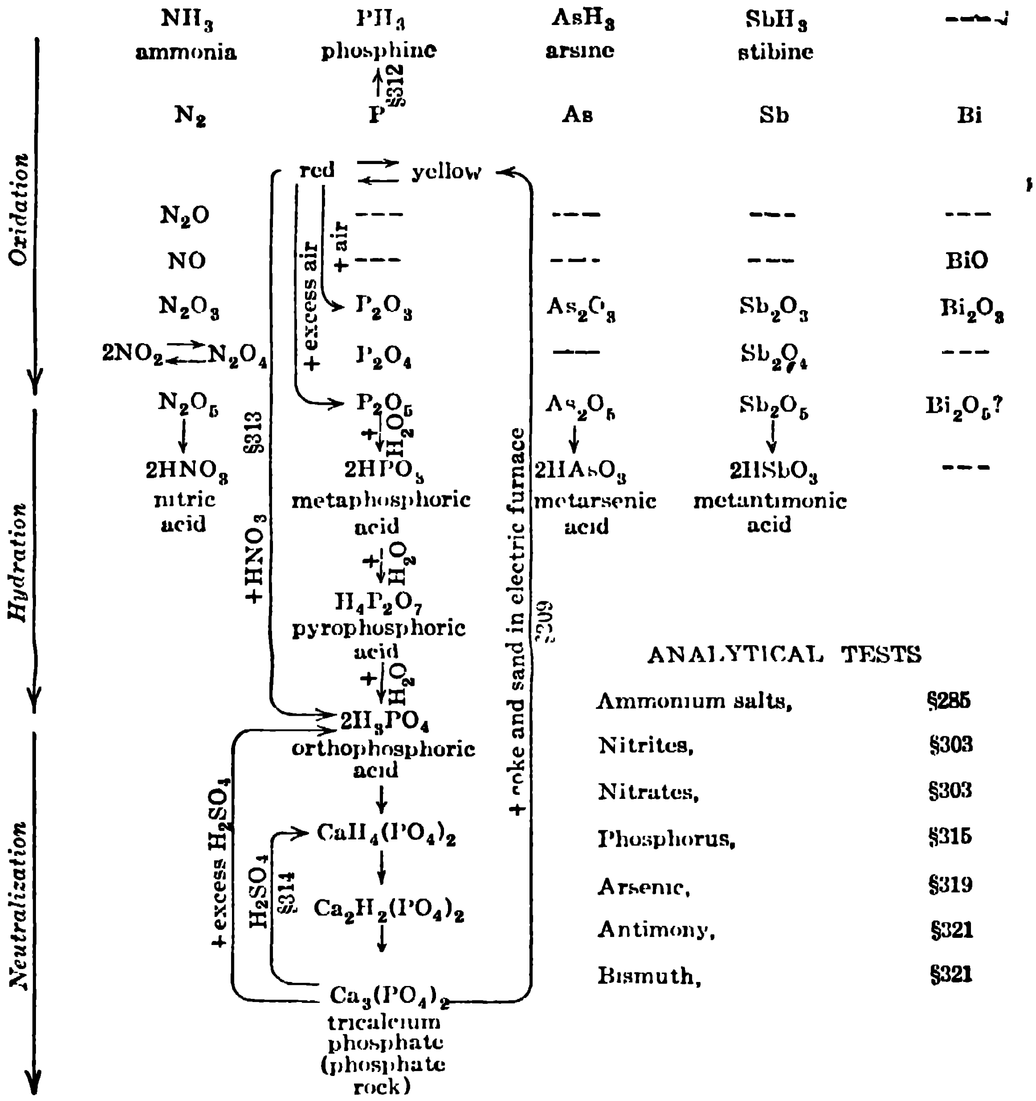
FIG. 77a.—Research in analytical chemistry, University of Michigan. A new method for determining antimony in alloys.

322. Uses of Antimony and Bismuth.—Antimony is one of the few substances which resemble water in expanding when they solidify. Its alloys with lead have the same property, and are accordingly used for *type metal* (Pb, 82; Sb, 15; Sn, 3); the expansion forces the alloy into every minute detail of the mold, and gives a much sharper casting than could be obtained with such an alloy as brass. Antimony is also used in small quantities to toughen and harden lead, for storage-battery grids, piping, gutters, etc.

Babbitt-metal, or *anti-friction alloy*, contains tin, copper and antimony (Sn, 75; Sb, 12; Cu, 13). Its value depends on the fact that the solidified alloy consists of hard crystals, which take up most of the pressure, imbedded in a supercooled liquid which is yielding enough to distribute the pressure and make automatic adjustment for wear.

Bismuth is obtained commercially, as a by-product, in the electrolytic refining of lead (§ 574). It is contained in small percentages in a good many anti-friction alloys, but is chiefly used in *fusible alloys* for electric fuses, plugs for automatic fire-alarms and automatic sprinkler systems, and as *stereotype metal.* Most of these fusible alloys contain about 50 per cent bismuth, with smaller amounts of lead and tin, and sometimes cadmium (i.e. Wood's metal: 4 parts of Bi; 2 of Pb; 1 of Sn; 1 of Cd; m.p. about 60° C.).

323. Graphical Summary.



ANALYTICAL TESTS

Ammonium salts,	§285
Nitrites,	§303
Nitrates,	§303
Phosphorus,	§315
Arsenic,	§319
Antimony,	§321
Bismuth,	§321

EXERCISES

1. Name the following compounds and give the valence of the non-metal other than oxygen contained in each:

K_2HPO_4, KH_2PO_3, NH_4PO_3, H_3PO_3, $Ca(MnO_4)_2$, $K_2S_2O_7$, $Mg_2P_2O_7$, $Na_2Cr_2O_7$, PH_3, $NaNO_2$, $CaSiO_3$.

2. How would you convert:

HNO_3 into NO	SO_2 into H_2SO_4
H_3PO_4 into HPO_3	$NaHSO_4$ into Na_2SO_4
H_2S into S	SO_2 into $NaHSO_3$

3. Which of the changes in the preceding question are oxidation, which reduction, which neither?

4. Write and balance the equation for the reduction of metaphosphoric acid to phosphorus, by means of carbon.

5. Use your knowledge of the chemical properties of the substances concerned to write equations for:

(*a*) Oxidation of red phosphorous to orthophosphoric acid by concentrated nitric acid;

(*b*) Action of a solution of sodium metaphosphate on one of silver nitrate;

(*c*) Heating secondary ammonium phosphate with an excess of sodium hydroxide;

(*d*) Formation of insoluble calcium pyrophosphate from a solution of sodium pyrophosphate.

6. What reagents are used in testing for chlorides, sulfates, ammonia, nitrates, phosphates?

What *ions* are tested for? Write ionic equations to illustrate the first four cases.

7. How would you test for:

(*a*) Chlorine in potassium chlorate;

(*b*) carbon in cane sugar;

(*c*) phosphorus in yolk of egg;

(*d*) sulfur in hard rubber.

8. From the properties of the substances concerned, formulate the following reactions:

(*a*) Burning phosphine in air.

(*b*) Oxidizing pyrite with concentrated nitric acid.

(*c*) Dissolving phosphate rock in hydrochloric acid.

(*d*) Dissolving sodium carbonate in a large excess of phosphoric acid.

(*e*) Burning an ordinary match, containing potassium chlorate.

9. How much iodine is needed to convert 10 g. of red phosphorus into orthophosphoric acid, by the reaction of § 191.

10. How many liters of air are needed to burn 3.1 g. of phosphorus to phosphorus pentoxide?

11. From the known properties of the substances concerned, make a reasonable formulation of the following reactions:

(*a*) Paris green is dissolved in hydrochloric acid;

(*b*) Arsine is oxidized by nitric acid to arsenic acid;

(*c*) Arsenic pentoxide is dissolved in an excess of potassium hydroxide;

(*d*) Arsenic acid oxidizes hydrochloric acid;

(*e*) Magnesium ammonium arsenate is ignited, expelling ammonia and water, and leaving behind a residue of magnesium pyroarsenate;

(*f*) Arsenic trioxide is boiled with nitric acid.

12. What is the molecular formula of arsenic (§ 162) if a liter of its vapor, recalculated to standard conditions, weighs 13.7 g.?

13. Write the formulas of: stibine, calcium metarsenite, sodium metantimonate, basic antimony nitrate, bismuth acetate, bismuth phosphate, arsenious sulfide, phosphorous acid.

14. Write molecular and ionic equations for the reaction which you believe will take place when a solution of arsenious acid is oxidized with bromine.

CHAPTER XXIV

CARBON

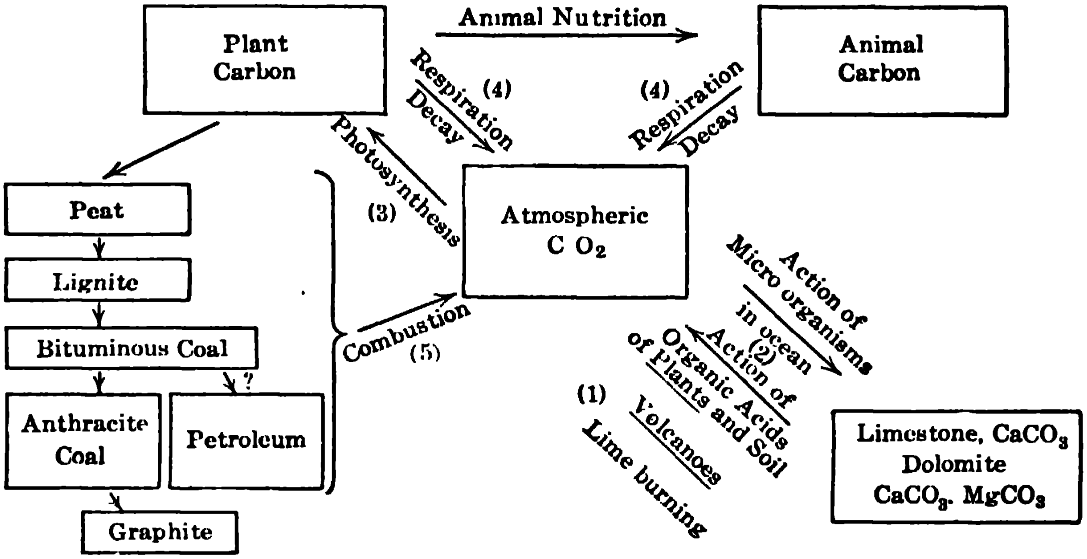
324. Organic Chemistry.—The element carbon is remarkable for the immense number of compounds that it forms. Listed about 30 to a page, these occupy over 4700 pages in a great reference catalogue, Richter's *Lexikon* (4 vols., 1910). With recent additions, the number of carbon compounds known is fully 200,000 —about twice as many as have been discovered for all the other elements together. This overwhelming profusion of material is the present justification for the practice of giving a special name, **Organic Chemistry,** to the chemistry of the compounds of carbon.

However, this great number of compounds need not cause dismay; for the field of organic chemistry has the advantage of being beautifully systematic. The hosts of carbon compounds are marshaled, as by regiments and companies, into groups and sub-groups of related compounds. A knowledge of the properties of a very limited number of individuals—a few in each group, serving as types for the rest—thus suffices to give one a very fair idea of the general aspect of the science. An organic chemist has much the same knowledge of his subject that a forest ranger has of a forest; he recalls the chief features of the landscape, and the principal roads and trails, though he may not know many of the individual trees.

325. The Cycle of Carbon in Nature.—Every important country of the globe contains inexhaustible supplies of the important carbonate minerals, **limestone, chalk, and dolomite** (see §§ 447, 453).

These have been produced from the calcareous skeletons of living organisms that swarm in the water of the ocean, from the Arctic to the Equator, in all but the most extreme depths: corals; sponges; shellfish, large and small; and a myriad of microscopic forms. The remains of these forms of life make up a large part of the sediment that covers the ocean bottom to great depths, over more than half the surface of the earth. Most of the present land areas are covered with sedimentary rocks, derived from deposits of such material uplifted from the beds of former oceans.

Carbon, like nitrogen (§ 305), tends to run through a definite cycle in nature:



1. By volcanic action, and by such human activities as the "burning" of limestone to form quicklime (§ 455) and the production of pig iron in a blast furnace (§ 492), vast quantities of carbon dioxide are returned to the atmosphere. The action of the organic acids of plants on the limestone of the soil releases further quantities.

2. These processes are opposed by the activity of the organisms responsible for the formation of chalk and limestone beds in the depths of the ocean.

3. Plants withdraw vast quantities of carbon dioxide from the atmosphere, and build it up into complex organic compounds of the most diverse sorts, at the expense of the energy of sunlight. This process is called **photosynthesis.**

4. The respiration of plants and animals, and their decay after life has ceased, restore carbon dioxide to the atmosphere, and thus tend to counterbalance photosynthesis.

5. Plant material of former geological ages, compacted and chemically altered by pressure and heat, has produced coal. By burning this, we now restore vast quantities of carbon dioxide to the atmosphere, from which it was long ago abstracted by photosynthesis. Thus the heat and light of burning coal represent energy stored up in the leaves of green plants, from sunlight that fell upon the earth perhaps half a million years ago.

It is possible that carbon dioxide is being withdrawn from the atmosphere by the formation of chalk beds and by photosynthesis more rapidly than it is being restored by all opposing processes; but this loss tends to be made good from the store of carbon dioxide dissolved in the ocean, which is estimated to be as much as forty times the total amount contained in the air. Thus it seems likely that the composition of the atmosphere has not changed much since present races of men first appeared upon the earth.

326. Amorphous Carbon.- When wood, coal, or bone is heated in a retort, closed to exclude the air, its chemical constituents are completely decomposed, various gases and volatile liquids are given off, and **amorphous** (i.e., non-crystalline) carbon remains behind. The process is called **destructive distillation.**

Amorphous carbon thus prepared is always far from pure, for it contains all the mineral constituents (ash) of the original material, as well as several per cent of oxygen and hydrogen. The principal forms of amorphous carbon are *wood charcoal, coke* (from coal), *bone-black* (= animal charcoal), and *lamp-black*.

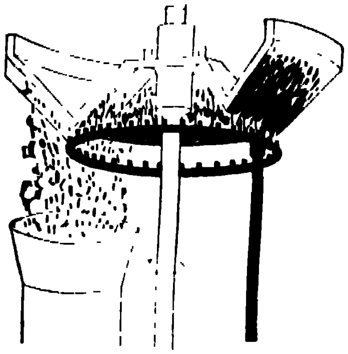


FIG. 78 —Lamp-black

Lamp-black (oil-black or gas-black) is made by burning fats, oils, or natural gas in a limited supply of air, under a revolving, water-cooled trough, of V-shaped cross-section (Fig 78). It is used for printers' ink, black enamels, for filling rubber (§ 353), and as a heat-insulator, for surrounding small furnaces.

327. Adsorption.—Charcoal made from fruit pits and cocoanut shells is dense but highly porous, and is used in gas masks for absorbing poisonous gases. Its value depends on its porous nature, which gives it an enormous surface, to which the molecules of gas tend to cling. If the gas is a readily condensable one, such as ammonia, it is attracted so strongly to the carbon surface that it is condensed to a liquid film, several molecules thick. The process is called **adsorption.** A good sample of charcoal will adsorb several hundred times its own volume of ammonia.

Charcoal, to be used in gas masks or in gasoline recovery (§ 345), needs to be "activated" by treatment at a white heat with superheated steam. This increases the capacity of the material for adsorbing gases, presumably by the destruction of tarry substances that tend to clog the pores of the untreated charcoal.

Bone-black, another highly porous material, is often used to adsorb and remove coloring matter from sugar solutions, in the manufacture of white sugar (§ 367). Adsorption also plays a part in analytical chemistry; for solutions being filtered often lose a part of their dissolved material, through adsorption by the filter paper; and precipitates are often rendered impure by salts adsorbed from the solutions in which they are formed.

328. Coke.—A few years ago, much coke was produced in the United States in old-fashioned "bee-hive" coking ovens, and the volatile products (coal gas, tar, benzene, and ammonia) were burned or discharged into the atmosphere. But the Great War brought such an enormous demand for ammonia to be transformed into nitric acid (§ 298) for the manufacture of muni-

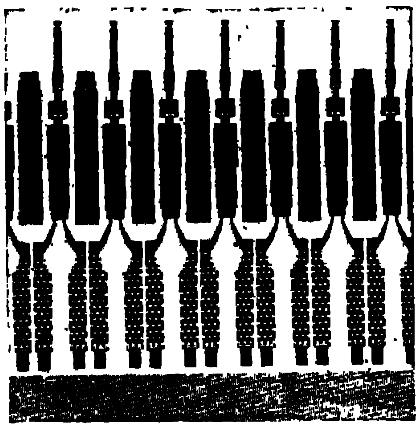


Fig. 79.—Cross-section of a row of by-product ovens. The larger rectangular areas are the ovens, which are arranged alternately with somewhat smaller chambers, in which air and gas mingle and burn with an intense flame. Below the retorts are chambers filled with brickwork, for preheating the gas and air (as described in § 497).

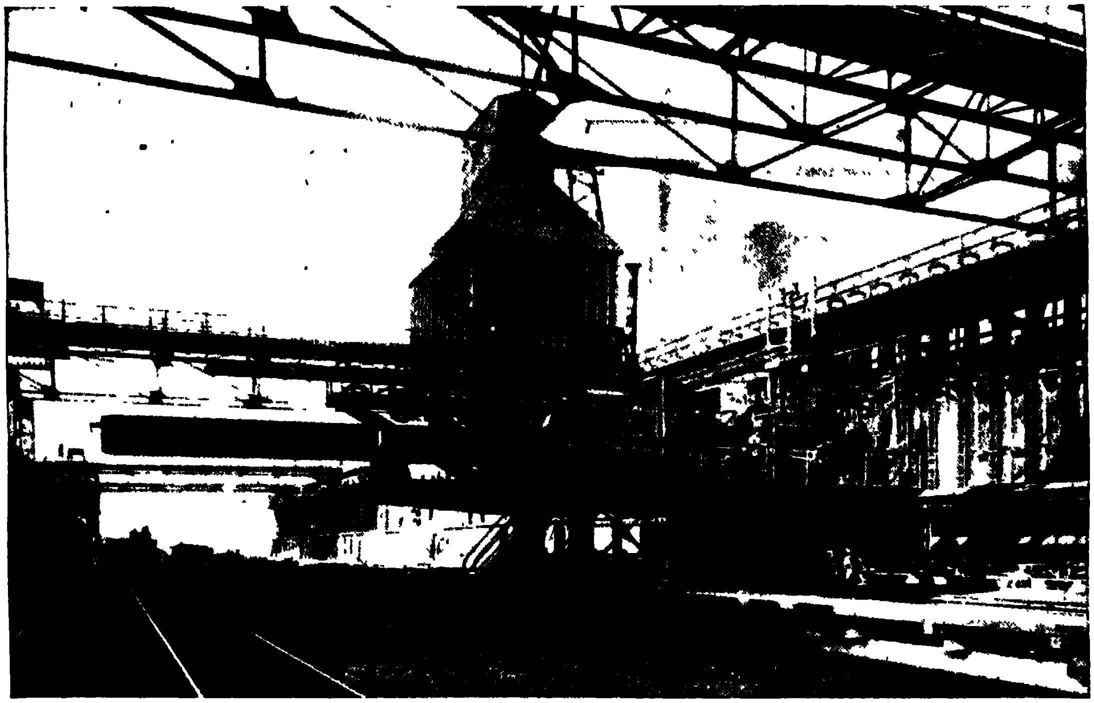


Fig. 80.—A row of by-product ovens. When an oven is ready to be discharged, the doors are opened and the white-hot coke pushed out by means of the long horizontal beam, shown on the apparatus in the foreground, and immediately quenched with a stream of water.

tions, that within the four years the industry was revolutionized by the installation of **by-product ovens** (Fig. 79), permitting the recovery of the ammonia and benzene formerly wasted.

Coke is somewhat less porous than charcoal, and contains from 5 to 20 per cent ash. Its density and hardness depend on the kind of coal from which it is made, and the temperature reached in the coking process. Metallurgical coke, used in reducing iron from its ores, needs to be very dense and hard, to resist crushing under the weight of the layers of ore and limestone charged in above it in the blast furnace (§ 491). The United States now produces over 60,000,000 tons of metallurgical coke each year (1921), over half of which comes from by-product ovens.

329. Graphite.—When coke or anthracite coal is heated to a high temperature in an electric furnace (Fig. 81), it is converted into **graphite,** a soft, flaky, grayish-black, fairly crystalline form of carbon, several times as dense as charcoal (apparent density of graphite 2.50; of charcoal, 0.39 to 0.65). Ferric oxide, present in small amounts in the ash of the coke or added to the charge in the furnace, serves to catalyze the transformation of amorphous carbon into graphite.

Graphite differs from the other forms of carbon in being a *conductor of electricity.* Thus it finds important application in preparing copper electrotypes (§ 533). Graphite molded into rods with tar, and baked at a high temperature, forms arc-light carbons or furnace electrodes. Graphite in colloidal suspension in oil or water (**gredag, aquadag**), is used as a lubricant.

Veins of **natural graphite** are found in a number of parts of the world; the best grades come from Ceylon. This material is ground, mixed with clay, and molded into pencil-leads or crucibles (for melting metals).

330. Diamond.—If considerable carbon is dissolved in molten iron, a portion will crystallize out as graphite when the iron solidifies, and may be recovered by dissolving the metal in acid. But when molten iron is quenched in cold water, the outer portion solidifies first, and, in contracting, exerts an enormous pressure on the rest. *Moissan,* the discoverer of fluorine (§ 179). showed that under these circumstances carbon dissolved

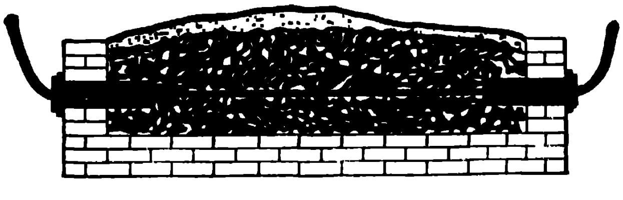


Fig. 81.—A graphite furnace. Graphite rods, buried in the center of a mass of coke, serve to conduct the electric current until the surrounding material has become graphitized.

in the iron separates as a fine powder, consisting in part of true diamonds.

This process is of no commercial value, for the gems thus produced are never of much more than microscopic size; but it helps us to understand that diamonds must have been formed in nature by slow crystallization from iron or molten rock at very high temperatures, and under enormous pressures. The diamond is, in fact, in an unstable condition at atmospheric pressure, tending to pass over into graphite. If this change were not imperceptibly slow, at ordinary temperatures, diamonds would soon lose their reputation for being a safe investment. At temperatures approaching a red heat, graphitization takes place very rapidly.

Most of the diamonds now mined come from South Africa. Their occurrence there, in and near volcanic pipes, supports the theory just given concerning their origin. The diamond is the hardest substance known, though closely rivaled in hardness by the mineral corundum (Al_2O_3) and the carbides of boron and silicon, (B_4C_3 and SiC). Imperfect diamonds, Brazilian black diamonds (*carbonado*), and fragments from the cutting of rough diamonds in the manufacture of gems are used in drilling rock. Without diamond rock-drills, the Panama Canal and our Rocky Mountain tunnels might never have been built.

The brilliance of the diamond is due to its high index of refraction for light, which causes most of the rays that enter it to be reflected from the interior. This property is enhanced by skillful cutting.

331. Properties of Carbon.—The different forms of carbon differ in color, density, and hardness, but are identical chemically, as is shown by the fact that they all burn in oxygen to form CO_2. Carbon cannot be melted; but at about 3600° C. it vaporizes or sublimes. This is, therefore, the maximum temperature obtainable with an electric arc struck between carbon terminals.

Carbon is quite *inert* at ordinary temperatures, and is unaffected by boiling with dilute acids and alkalies. Such vigorous oxidizing agents as boiling concentrated nitric and sulfuric acids dissolve amorphous carbon slowly. Carbon unites directly, at high temperatures, not only with oxygen, but with most metals and many non-metals. When CaO, SiO_2, and many other oxides are heated with coke in an electric furnace, they are first reduced to the free element, which then unites with the excess of carbon to form a carbide. Thus are produced **silicon carbide** or **carborundum** (§ 414) and **calcium carbide** (§ 457).

332. Testing Fuels with a Calorimeter.—The heating values of fuels are commonly determined by burning them in a **bomb-calorimeter.**

This consists of a thick-walled cylindrical vessel or bomb (Fig. 82), lined with platinum, or constructed of a specially resistant alloy (illium, § 525) and closed with a heavy screw-cap.

A carefully weighed sample of the substance to be burned is placed in the small platinum cup at *A*, in contact with a fine iron wire, which is connected, through two heavy conductors and the terminals at *B*, with a pair of storage cells. Pure oxygen, under a pressure of about 20 atmospheres, is introduced through the valve *V*, at the top. The bomb is then immersed in a known quantity of water, in a covered, insulated vessel supplied with a delicate thermometer, as shown in Fig. 83.

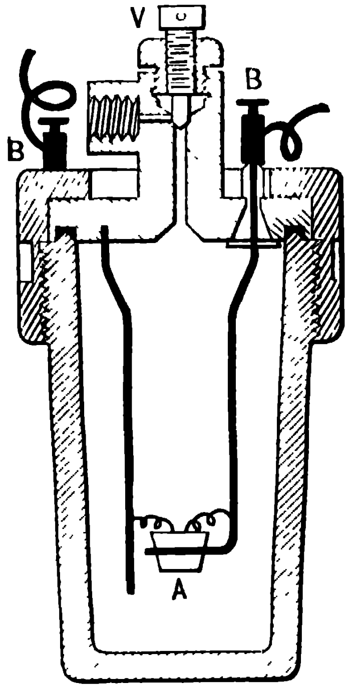


Fig. 82 —Cross-section of calorimeter bomb.

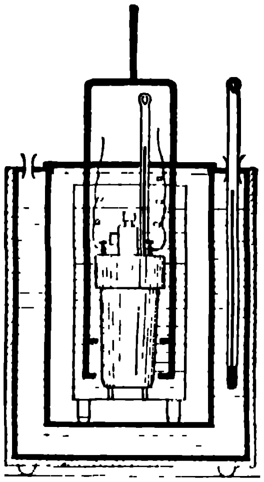


Fig. 83 —Cross-section of calorimeter, showing bomb in place.

When all is ready, the combustible substance within the bomb is ignited by closing the circuit for a moment. In the presence of the compressed oxygen, it burns away almost instantly, liberating a definite quantity of heat, which is conducted through the walls of the bomb, and raises the temperature of the water.

After the water has been stirred for several minutes, the maximum rise in temperature may be noted. From this and the weight of water used, it is easy to calculate how many calories of heat are liberated by the burning. This, of course, calls for corrections, not only for the heat liberated by the combustion of the fine iron wire but also for that absorbed by the bomb, stirrer, and calorimeter jacket, or lost by radiation (see Fig. 95).

333. Carbon Dioxide.—Carbon dioxide gas is produced on a commercial scale, for liquefaction, (1) **by alcoholic fermentation** (§ 357); (2) **by burning carbon with an excess of air; and** (3) **by limestone burning** (§ 455). It is about one and a half times as heavy as air, and fairly soluble in water (about 100 vols. in 100 at 15° C., and 1 atmosphere). It is easily liquefied by pressure alone.

Carbon dioxide is quite stable at low temperatures, but at a white heat it is partially decomposed into carbon monoxide and oxygen:

$$2CO_2 \rightleftarrows 2CO + O_2 - 58{,}300 \text{ cals.}$$

Solutions of carbon dioxide in water are assumed to contain *carbonic acid*, H_2CO_3. This is itself unknown, but forms two series of salts, acid carbonates or bicarbonates (such as $NaHCO_3$), and normal carbonates (such as Na_2CO_3 and $CaCO_3$). These will be discussed hereafter in connection with the other commercially important compounds of the metals concerned.

The chief uses of carbon dioxide are (1) the manufacture of bottled carbonated drinks; (2) the preparation of soda by the Solvay process (§ 437); (3) the preparation of white lead (§ 580); (4) fire extinguishers.

The common household fire-extinguisher contains a bottle, which may be broken or turned upside down, spilling sulfuric acid into a solution of sodium bicarbonate. *Foamite fire-foam* is a froth of carbon dioxide bubbles, stabilized (§ 390) by aluminum hydroxide, together with a small amount of some organic substance. This has been used very effectively to extinguish fires in burning oil-tanks.

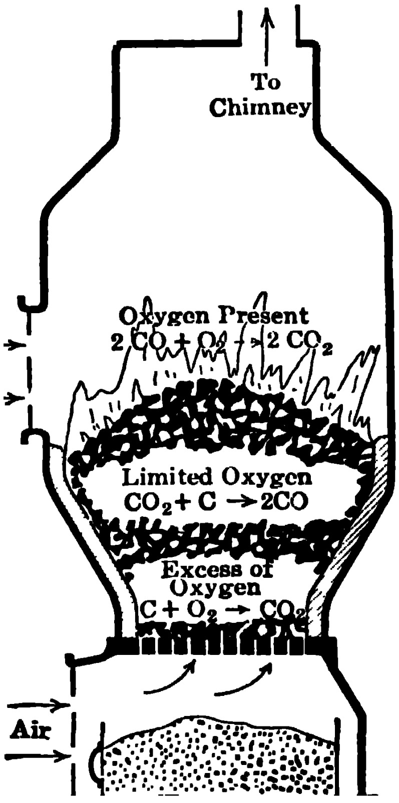

To Chimney
Oxygen Present
$2CO + O_2 \rightarrow 2CO_2$
Limited Oxygen
$CO_2 + C \rightarrow 2CO$
Excess of Oxygen
$C + O_2 \rightarrow CO_2$
Air

FIG. 84.—Formation and combustion of carbon monoxide, in a stove or furnace.

334. Carbon Monoxide. — 1. In the bottom of a stove or furnace, just above the grates (Fig. 84), carbon burns to carbon dioxide. As this passes upward through the bed of red-hot fuel, it is reduced to carbon monoxide:

$$CO_2 + C \rightleftarrows 2CO - 39{,}000 \text{ cals.}$$

(Notice that this reaction absorbs heat). If air is admitted above the solid fuel, through openings in the fire-doors, the carbon monoxide there burns to carbon dioxide, with a pale blue flame.

2. Carbon monoxide is prepared commercially by passing air (or a mixture of carbon dioxide and oxygen) upward through a deep bed of incandescent coke.

Why not use pure oxygen (56). ? Pure carbon dioxide?

3. Carbon monoxide is the most important **reducing agent** known to industry. Iron ore, for example, in the upper part of the blast furnace (§ 492), is reduced to metallic iron:

$$Fe_2O_3+3CO \rightleftarrows 2Fe+3CO_2+8{,}400 \text{ cals.}$$

A number of other useful metals are obtained in a similar way.

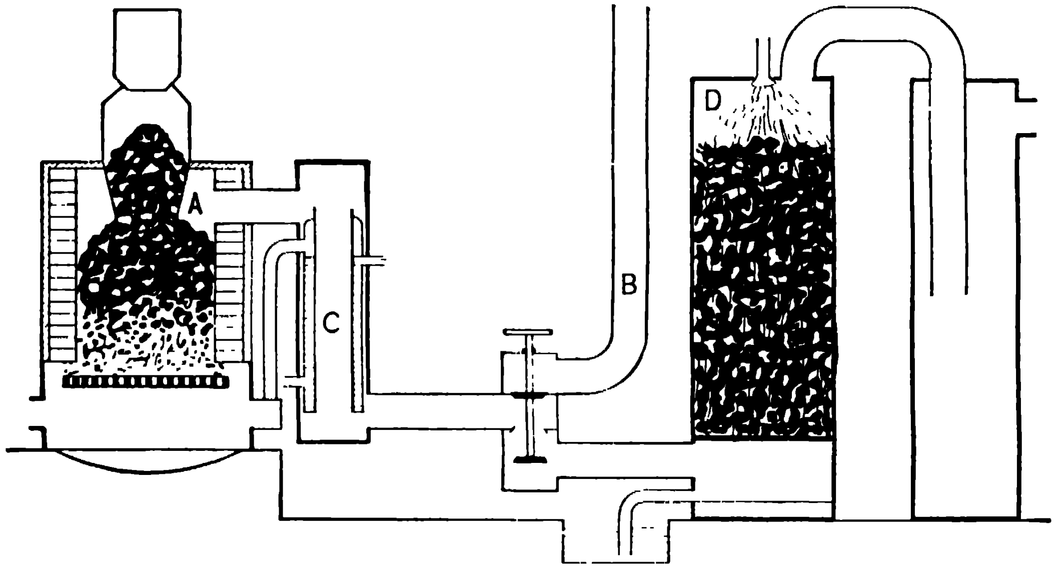


FIG. 85.—Diagram of a plant for making producer-gas.

If carbon monoxide lacked this property we should still be living in the Stone Age.

4. Carbon monoxide is **extremely poisonous,** uniting directly with the red blood corpuscles, and thus preventing them from absorbing oxygen; but prompt breathing of large quantities of fresh air, or the use of oxygen in a pulmotor, may displace the carbon monoxide and overcome the poisoning.

Explain this as a case of "mass action" (§ 217).

Carbon monoxide is not very readily condensable, and charcoal-filled gas-masks (§ 326) are therefore no protection against it (an absorbent is mentioned in § 208).

335. Producer Gas.—By burning coal in a gas-producer with a limited supply of air, we obtain producer gas, a mixture containing about 60 per cent N_2, 30 per cent CO, and 10 per cent H_2 and hydrocarbons.

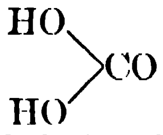
The supply of air is forced through the producer shaft (*A*, Fig. 85) by a fan or small compression-pump, or is drawn through by suction created by an explosion engine using the finished gas as fuel. After traversing a water-cooled condenser (*C*), the gas passes up a coke-tower (*D*) in which it is purified by a spray of water. This takes out tarry impurities, which would otherwise cause carbon troubles in the engine. A by-pass (*B*) leading to a chimney, creates a draft for starting, and is closed when the producer has become hot enough to yield combustible gas. Very often, such a furnace is made to yield a mixture of producer gas and water gas (§ 69), by passing both air and steam through the charge of coal, in alternate periods of ten or fifteen minutes each.

The gas-producer is the most economical means of using slack coal, or coal containing too high a percentage of ash to burn on ordinary grates; for carbon monoxide has almost as great a fuel value as the carbon from which it comes, and may be burned more efficiently in explosion engines than coal under a steam boiler. As our supplies of high-grade coal become more and more depleted, producer gas will become more and more important. In the future, the energy of coal, through the gas-producer, explosion engine, and electrical generator, may perhaps be converted into electrical energy, at the mine itself, for transmission to distant points over high-tension lines.

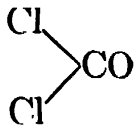
336. Phosgene and Urea.—When chlorine and carbon monoxide are passed together over charcoal as a catalyzer, they unite to form **phosgene,** or carbonyl chloride, $COCl_2$. This is an intensely poisonous, volatile liquid (B.P. 8° C.). It is the most important of the toxic military gases, and is now used in considerable quantities in the manufacture of dyes.

When phosgene is treated with ammonia, the two chlorine atoms are replaced by two **amino groups** ($-NH_2$), giving a white crystalline solid, **urea,** $CO(NH_2)_2$. This is of historical interest as being the first organic compound to be synthesized in the laboratory from materials not themselves derived from living plants and animals (1828). Urea is the principal form in which waste nitrogen is eliminated from the body, through the kidneys. An adult person excretes about 30 grams in a day.

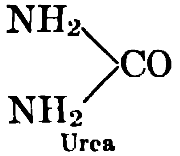
Notice the close relationship between these three substances:



Carbonic acid



Phosgene



Urea

337. Carbon Disulfide.—When sulfur vapor is passed over red-hot carbon in an oil-fired or electric furnace, the product is carbon disulfide (or bisulfide), a colorless, volatile, highly refractive liquid. **Its vapors are dangerously explosive when mixed with air, and so inflammable that they may be ignited by a hot glass rod.** Carbon bisulfide is an excellent solvent, employed for extracting oils from seeds, for vulcanizing rubber and for manufacturing " artificial-silk " (§ 370). Farmers frequently pour small amounts into the tunnels of rodents, or into tight boxes containing insect-infected seeds—thus taking practical advantage of the volatility and poisonous properties of the liquid.

338. Cyanogen, Hydrocyanic Acid, and the Cyanides.—Gas produced by the destructive distillation of coal (§ 283) contains not only ammonia but a number of other compounds of nitrogen, including traces of **cyanogen, $(CN)_2$**, a poisonous, readily condensable gas. This is removed in the purification of the coal gas as **potassium ferrocyanide, $K_4Fe(CN)_6$** (yellow crystals, § 505). When this salt is heated it is decomposed, yielding **potassium cyanide, KCN:**

$$K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2.$$

The cyanides are **intensely poisonous** substances, salts of **hydrocyanic acid, HCN.** Potassium and sodium cyanides are used in extracting gold from its ores (§ 546).

Hydrocyanic acid itself (sometimes called prussic acid) is an *intensely poisonous* volatile liquid (b.p. 26° C.) prepared by distilling cyanides with dilute sulfuric acid:

$$KCN + H_2SO_4 = KHSO_4 + HCN \uparrow .$$

It is an *extremely inactive* acid, and sodium and potassium cyanides accordingly react alkaline toward litmus (§§ 114, 269). Even the carbonic acid of the atmosphere will displace hydrocyanic acid from its salts; hence one should take care never to inhale the vapors from a cyanide solution.

EXERCISES

1. What is the purpose of the clay in crucibles and lead pencils?

2. From the stated solubility of carbon dioxide (§ 333) and the Law of Henry (§ 128) calculate the weight of carbon dioxide held in solution in one liter of a carbonated drink, under a pressure of 30 lbs. per square inch above atmospheric pressure, neglecting the formation of carbonic acid.

3. From the composition of air by volume (§ 280) calculate the percentage of CO in a fuel gas made by passing air through a bed of white-hot coke.

4. Assuming the proteins (§ 388) to contain an average of 16 per cent nitrogen, what weight of protein is represented by a daily excretion of 30 g. of urea?

5. What weight of sodium cyanide, 90 per cent pure, is needed to produce 1 cu. m. of hydrogen cyanide gas?

6. Which gives vapors of the higher density, carbon bisulfide or phosgene, and in about what ratio?

7. What weight of coke, containing 10 per cent ash, is needed to produce 1000 cu. m. of carbon monoxide, at standard conditions (§ 147)?

8. What volume of air at standard conditions is needed to burn 1 lb. of pure carbon to produce carbon dioxide (§ 147)?

9. Draw up a table of the uses of the different forms of carbon, based on material obtained from the encyclopædia, or a chemical dictionary.

10. Enumerate the elements thus far studied that exist in two or more allotropic forms.

11. How can air be freed from carbon dioxide? Tell how the percentage of carbon dioxide in the air is determined.

12. How much anhydrous sodium carbonate is needed to prepare a liter of carbon dioxide gas, dry, at 40° C., and 740 mm. barometric pressure?

13. Describe two methods, different in principle, for obtaining carbon dioxide from limestone. How could you use one of these methods to determine the percentage of limestone in a mixture of limestone and clay?

14. How could you separate the two gases in a mixture of carbon monoxide and carbon dioxide, and obtain both of the gases in a pure condition?

15. What volume of water gas (§ 69) can be obtained from 12 g. of carbon? What volume of air (assumed one-fifth oxygen by volume) is needed to completely burn this volume of water gas?

16. What volume of carbon dioxide gas is needed to react with the barium hydroxide contained in 1 liter of N/5 solution to form a precipitate of barium carbonate?

CHAPTER XXV

HYDROCARBONS

339. Sources of the Hydrocarbons.—Compounds containing *carbon and hydrogen only* are known as **hydrocarbons.** The most important natural sources of these are **natural gas, petroleum, coal gas, coal tar,** and the sap (**turpentine, rubber**) from certain species of trees. These all consist of mixtures of hydrocarbons, with smaller amounts of other substances. Altogether, several thousand different hydrocarbons are known.

340. Unsaturated and Saturated Hydrocarbons.—Many hydrocarbons *unite directly* with hydrogen or a halogen (often only in the presence of a catalytic agent). These are the **unsaturated hydrocarbons:**

$$\underset{\text{Acetylene}}{C_2H_2} + 2Cl_2 = \underset{\text{Acetylene tetrachlorid}}{C_2H_2Cl_4}.$$

Other hydrocarbons are **saturated.** They will not unite directly with either hydrogen or the halogens; though chlorine or bromine will *replace* hydrogen (*substitution*):

$$\underset{\text{Methane}}{CH_4} + Cl_2 = \underset{\text{Methyl Chloride}}{CH_3Cl} + HCl.$$

The *chlorinated hydrocarbons*, prepared from unsaturated hydrocarbons by direct addition, from saturated hydrocarbons by substitution, and in various other ways, include chloroform, $CHCl_3$, and a number of other useful substances (carbon tetrachloride, CCl_4; acetylene tetrachloride, $C_2H_2Cl_4$; etc.). They are valuable solvents for fats and oils, and have the advantage over gasoline and carbon disulfide of being non-inflammable (dry cleaning).

341. The Paraffin Series.—If **natural gas,** or the lower-boiling portion of American petroleum, is subjected to elaborate and repeated fractional distillation, it can be separated (rather imperfectly) into a series of closely related hydrocarbons. The first six are:

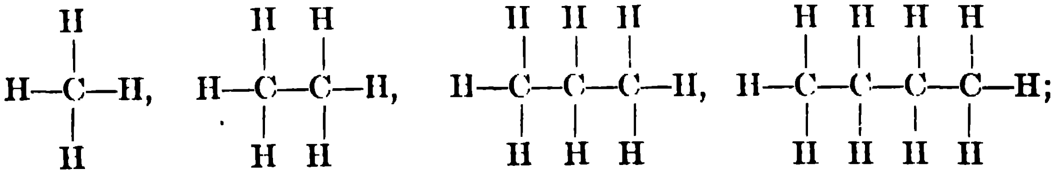
Methane,	CH_4	Gas,	B. P. −164
Ethane,	C_2H_6	Gas,	B. P. − 85
Propane,	C_3H_8	Gas,	B. P. − 37
Butane,	C_4H_{10}	Gas,	B. P. 1
Pentane,	C_5H_{12}	Liquid,	B. P. 38
Hexane,	C_6H_{14}	Liquid,	B. P. 71

Each of these formulas, after the first, may be derived from the preceding one by addition of CH_2.

Following hexane, other members of the series are known, without omission, as far as $C_{24}H_{50}$; and a few of still higher molecular weight. After the first four, the names are derived from Greek numerals. Thus, the eighth is octane, C_8H_{18}; and the tenth decane, $C_{10}H_{22}$. Notice the fairly regular increase of boiling point with increasing molecular weight. The first four members are gases at room temperature, the next twelve are liquids, and the following ones are solids.

The most conspicuous property of these paraffin or marsh gas hydrocarbons is their *chemical inertness*. Thus, kerosene and paraffin (both mixtures of these hydrocarbons) are not affected by prolonged boiling with concentrated sodium hydroxide or concentrated sulfuric acid; they are only very slightly affected by such vigorous oxidizing agents as concentrated nitric acid or chromic acid. Chlorine and bromine, however, act upon them readily (§ 340), *replacing* part or all of their hydrogen.

342. Structural Formulas of the Paraffin Hydrocarbons.—Review § 124. If carbon be considered as having a definite valence of four, then the only hydrocarbon we might expect to exist would be CH_4. To account for the numerous other hydrocarbons, it is necessary to assume that one or more of the four valences of any given carbon atom are employed in connecting it to other carbon atoms. Representing each unit of valence by a dash or dot (commonly called a *bond*), we may write the structural formulas of the first four paraffin hydrocarbons as follows:



$$H-\overset{H}{\underset{H}{C}}-H,\quad H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H,\quad H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H,\quad H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H;$$

otherwise written—

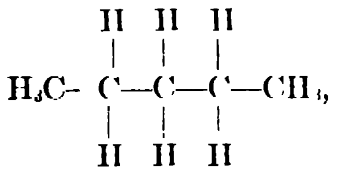
CH_4,	$CH_3\cdot CH_3$,	$CH_3\cdot CH_2\cdot CH_3$,	$CH_3\cdot CH_2\cdot CH_2\cdot CH_3$.
Methane	Ethane	Propane	Butane

It will be noticed that there are two hydrogen atoms attached to each carbon atom, with two extra hydrogen atoms at the two ends of the chain. Thus, for every n carbon atoms there are $2n+2$ hydrogen atoms, and **the general formula of the paraffin hydrocarbons is C_nH_{2n+2}.**

Only one hydrocarbon is known of the formula CH_4, one of the formula C_2H_6, and one of the formula C_3H_8; but there are two different butanes, C_4H_{10}, with entirely distinct properties, three different pentanes, C_5H_{12}, and a larger number still of hydrocarbons of higher molecular weight. The explanation is that the carbon atoms forming the more complicated molecules may be arranged or combined with one another in a number of different ways. Each of these different "architectural plans" results in a different kind of molecule, and accordingly in a different substance.

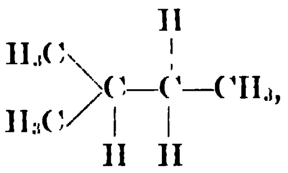
It is usually possible to tell which of several different possible plans corresponds to a given compound. The three pentanes, for example, have the structural formulas—

B.P. 38°

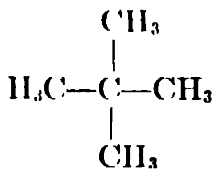


$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3,$

B.P. 30°



B.P. 9.5°.



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

Substances having the same percentage composition but different properties are called **isomers.** An important confirmation of the theory by which we account for their existence is found in the circumstance that no one has ever yet discovered more isomers of a given substance than corresponds to the different possible ways of arranging its atoms in space (while assigning to each element its customary valence). Isomers are known among inorganic compounds, but are not very common.

343. Petroleum.—Petroleum is a heavy viscous oil, greenish-brown to black in color. The world's annual production was about 97,000,000 tons in 1920, and is increasing very rapidly, by the opening of new deposits. At present, the United States furnishes about two-thirds of the whole; the other chief producers, in order, during the past twenty years, have been Russia, Mexico, the Dutch East Indies, and Roumania.

Petroleum varies greatly in quality according to locality. That coming from Pennsylvania and neighboring states consists largely of hydrocarbons of the paraffin series. When the more volatile portions are distilled off, it leaves behind a solid residue, which is paraffin. California petroleum contains larger quantities of nitrogenous compounds, and on distillation, leaves a residue of asphalt. That from Texas and Oklahoma is variable, but for the most part is intermediate in chemical composition between the Pennsylvania and California oils.

The petroleum obtained from the well is transported in tank-cars or pipe lines. After settling, to remove sediment and water, it is distilled from large horizontal iron stills, set in brickwork, and heated by a direct flame or superheated steam. If the oil contains more than traces of sulfur compounds, these are decomposed by heating in stills containing copper oxide, agitated by mechanical stirrers (CuS is formed—Frasch process). If the percentage of sulfur compounds is very high, they may often be removed by heating the oil with a solution of PbO in $NaOH$ (i.e., sodium plumbite, § 577).

344. Distillation of Petroleum.—Petroleum, after being purified as just described, is separated into a number of commercial products (themselves still mixtures of hydrocarbons) by a process of fractional distillation (§ 83). A preliminary distillation separates the petroleum into several fractions, which are purified by agitation with concentrated sulfuric acid, washed with water, and distilled again. The nature of the final products depends on the composition of the original petroleum; it varies also with the state of the market, since an effort is always made to increase the yield of the fractions for which there is the most demand, at the expense of the rest. In a general way, the products are as follows:

Petroleum ether,	B. P. 40°–70° C.
Naphtha	80°–120°.
Motor fuel (gasoline)	B. P. 60°–190°.
Kerosene	B. P. 150°–250°.
Fuel oil	B. P. 250°–350°.
Light lubricating oil	Distilled with superheated steam.*
Heavy lubricating oil	
Vaseline	
Paraffin	
Petroleum coke	

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* When a liquid not completely miscible with water (§ 93) is heated in a current of steam, it is volatilized at a temperature lower than its boiling point, for the vapor pressure of water is then added to its own vapor pressure, to aid in overcoming the pressure of the atmosphere.

345. Motor Fuel.—The United States now has about 6,000,000 automobiles (1922), and the demand for motor fuel (gasoline) is enormous. At an average of two gallons for each motor each day, the yearly consumption in this country would be more than four billion gallons.

1. The gasoline on the market, before the sudden rise of the automotive industry, was **distilled from petroleum** within a very narrow range, say from 60° to 90° C., like the special grades now used for airplane engines. At present the range has been extended to include less volatile hydrocarbons formerly marketed as kerosene, with boiling points ranging up to nearly 206° C.

2. A considerable amount of gasoline is now obtained from **natural gas.**

This is chiefly methane, with smaller amounts of other paraffin hydrocarbons of low molecular weight. It has been found in many different parts of the world, nearly always in association with petroleum. By cooling natural gas, after compressing it to 15 or 20 atmospheres, the heavier constituents—chiefly pentane and hexane—are condensed to form "*casing-head gasoline.*" Recently a method has been developed for extracting gasoline from natural gas by adsorption with *activated charcoal* (§ 326). In either case, the product is blended with the less volatile material obtained by the fractional distillation of petroleum.

3. A third important source of fuel for internal combustion engines is **fuel oil.**

This is a hydrocarbon fraction obtained in the distillation of petroleum with boiling point between about 250° and 350°. It is too non-volatile to make good illuminating oil (kerosene) but too light for lubricating oil. To convert it into motor fuel, the hydrocarbons that it contains must be decomposed to form those of lower molecular weight—a process called "cracking." Several methods are in use for accomplishing this result, but the most successful one is the *Burton process.*

Fuel oil is charged into large retorts and distilled under a pressure of 5 to 6 atmospheres. By this means the boiling point of the material is raised to a temperature at which decomposition takes place, producing about 30 per cent of volatile liquid products (mostly unsaturated hydrocarbons) suitable for blending with gasoline obtained directly by distillation of petroleum. In addition, considerable quantities of uncondensable gases are liberated. The undistilled residue, amounting to about two-thirds of the original material, may be burned under retorts or boilers with the aid of a jet of steam, in the same way as crude-oil.

346. Acetylene.—When calcium carbide (§§ 457, 284) is treated with water, **acetylene,** an important illuminant, is evolved:

$$CaC_2 + 2HOH = Ca(OH)_2 + C_2H_2 \uparrow.$$

This is a colorless gas, with a characteristic odor. It burns with a highly luminous flame. The oxy-acetylene flame used for cutting and welding metals (§ 59) reaches a temperature of about 2700° C. This is several hundred degrees higher than the oxy-hydrogen flame, and only exceeded by the electric arc (3600° C.).

Compressed acetylene is highly dangerous, for it may be exploded by shock or by catalytic action of impurities, decomposing into its elements. This difficulty is met by dissolving the gas in acetone (*prest-o-lite*). Traces of acetylene may be detected by bubbling coal gas or other mixed gases through an ammoniacal solution of cuprous chloride. An explosive red precipitate is formed, cuprous acetylide, Cu_2C_2.

347. Coal-Gas.—Destructive distillation of soft coal is the most important source, not only of ammonium salts (§ 283), but also of domestic fuel gas and of a group of hydrocarbons that serve as the starting point in the manufacture of nearly all the important dyestuffs.

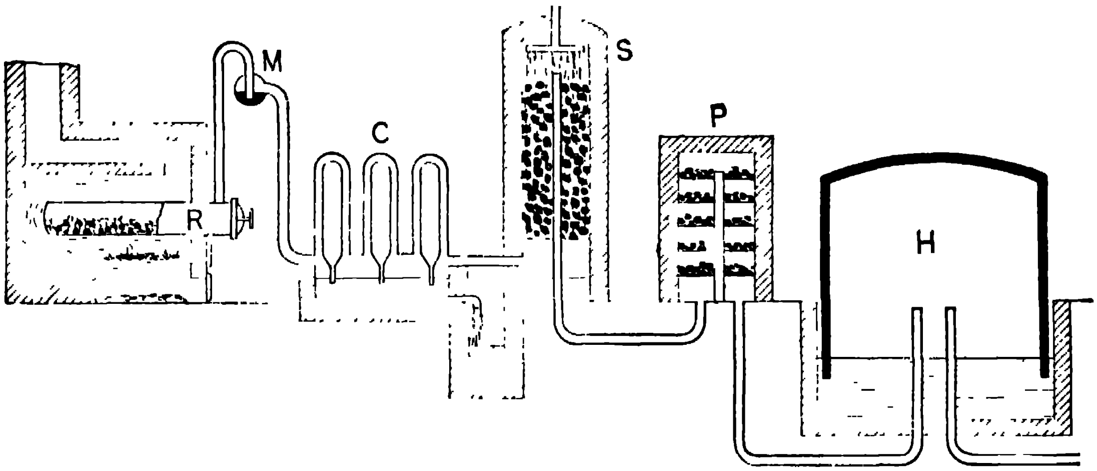


FIG 86 —Diagram of a plant for making coal-gas.

Figure 89 gives a simplified outline of a coal-gas plant, such as is found in almost every town and city. Coal is charged into closed retorts, *R*, of fused silica (§ 400) heated by direct flames. The volatile products bubble through water in a hydraulic main, *M*, where most of the solid and liquid products of distillation are separated (tar). The gas next passes to a series of cooling pipes, *C*, in which it is separated from a further quantity of tar. It then passes upward through a *scrubbing tower*, *S*, filled with loose coke over which water is sprayed. This dissolves and removes most of the ammonia and a part of the hydrogen sulfide. From the purifier, *P*, filled with quicklime or iron oxide, which takes out most of the remaining hydrogen sulfide, the gas passes to the storage-tank, or gas-holder, *H*, and thence to the distribution mains.

Purified coal-gas is about half hydrogen and one-third methane, with perhaps 10 per cent of carbon monoxide, and small percentages of unsaturated hydrocarbons and benzene vapors. It is these latter that are responsible for most of the luminosity of coal-gas, for methane and hydrogen burn with flames that are almost colorless. Coal-gas prepared as above is commonly mixed with an equal volume of water-gas (§ 69) before being distributed for domestic use through the city gas mains.

It is a fact of some practical importance that carbon monoxide and hydrogen burn with nearly colorless flames, while benzene vapor, acetylene, and unsaturated hydrocarbons in general give luminous flames. This is very easily explained. The latter substances are easily decomposed by heat, liberating finely divided carbon, which is speedily raised to incandescence. But the temperature has a great deal to do with the luminosity, for even a hydrogen flame will become luminous if the cylinder of the burner is heated from outside; while a coil of heavy copper wire, let down over a luminous flame, will decrease its luminosity. Ammonia burns in oxygen with a yellow flame, though it contains no carbon at all (§ 288).

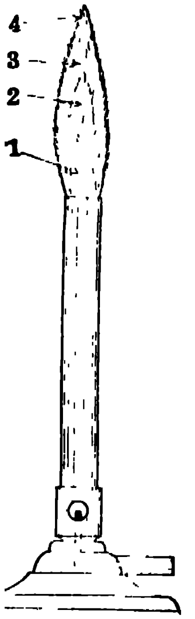


FIG. 87.

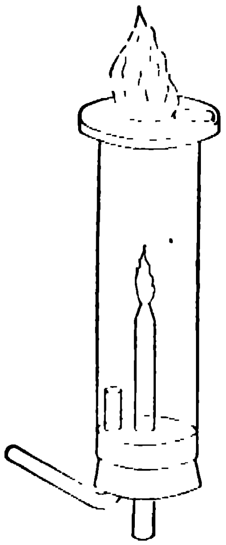


FIG. 88.

FIG. 87.—Structure of a Bunsen flame

FIG. 88.—A flame within a flame Below is a small flame of air, burning in an atmosphere of gas; above a larger one of gas, burning in air.

348. The Bunsen Flame.—If a Bunsen flame is rendered luminous by partly closing the holes at the base, three or four distinct cones are revealed, one within the other (Fig. 87). The innermost **colorless cone** (1) consists of a mixture of gas and air, which has not yet reached the kindling temperature. In the **bluish-green cone** (2), hydrogen and carbon monoxide are burning, liberating heat enough to decompose some of the unsaturated hydrocarbons, with the separation of carbon. In the **luminous cone** (3), carbon monoxide, hydrogen, and methane continue to burn; and as the incandescent carbon particles drift upward and outward, they too are consumed. The outer margin of this third cone marks the place of their complete disappearance. Finally, there is an **invisible cone** (4) in which the combustion of the carbon monoxide and hydrogen is completed, with the aid of oxygen withdrawn from the air surrounding the flame.

If more air is admitted at the base of the burner, the supply of oxygen is sufficient to consume the carbon particles at the instant of their liberation, and the flame is almost non-luminous. Yet even then there is an insufficient supply of air in the interior of the flame; and the gas in and just above the cone (2) will take oxygen from anything that can supply it—from oxides of the heavy metals, for example. This is therefore called the **reducing zone.** But the outer margin of the flame is an **oxidizing zone,** for there here a high temperature and a plentiful supply of oxygen.

The temperature of a flame is lowest (200° to 300° C.) in the innermost cone, and highest (1550° C.) just above the reducing flame; but such an extreme temperature is reached only locally. It takes a very good burner to heat the contents of even a small crucible above 1000° C.

In the blast-lamp (Fig. 88), compressed air and gas, led in by separate tubes, intermingle in nearly the right proportions for instantaneous and complete combustion. The flame is thus very much *decreased* in volume and correspondingly *increased* in temperature, and is actually several hundred degrees hotter than a Bunsen flame.

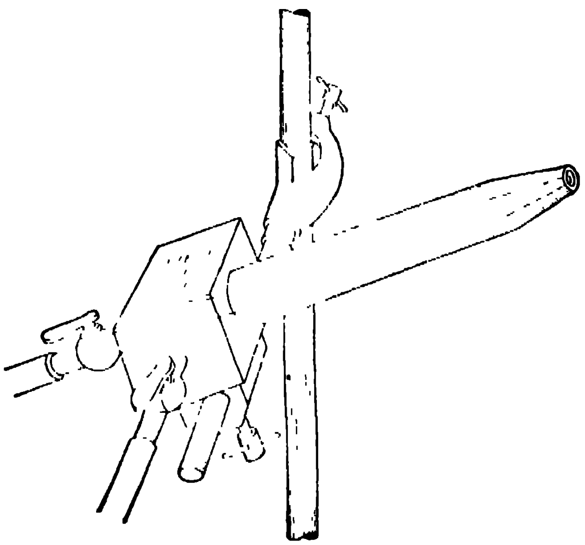


FIG. 89.—A blast lamp.

349. Some Thermochemical Calculations.—Review § 218. Thermochemical equations are of great assistance in calculations dealing with the heating value of fuels. The equation,

$$2C \text{ (graphite)} + O_2 = 2CO + 58{,}320 \text{ cals.}$$

indicates that 2 gram-atoms (=24 g.) of carbon, in the form of graphite, when burned in a limited supply of oxygen, produces

2 moles = 56 g. = 44.8 liters (at standard conditions) of carbon monoxide gas, liberating 58,320 calories of heat in the process. Such equations, when they deal with gases, are readily converted to the English system by remembering that 200 cu. ft. of any gas correspond to as many B.t.u. (Appendix H) as one mole corresponds to calories. Thus, in the case just considered, 2×200 = 400 cu. ft. of gas are produced for every 58,320 B.t.u. of heat liberated.

FIG. 90.—Towers for recovering benzene from coal-gas.

Thermochemical equations may be added or subtracted as if they were ordinary algebraical equations. Thus, let the equation,

$$2CO + O_2 = 2CO_2 + 136{,}100 \text{ cals.},$$

be added directly to the equation first given. We may then cancel out 2CO, which is common to both sides of the equation, and finally divide through by 2. Thus we obtain,

$$C + O_2 = CO_2 + 97{,}210 \text{ cals.}$$

for the heat liberated in oxidizing one gram-atom of carbon, directly to carbon dioxide. This illustrates the principle that if a chemical reaction takes place in several successive steps, the sum of the quantities of heat so liberated will be the same as if it had taken place in a single step. **(Law of Hess.)**

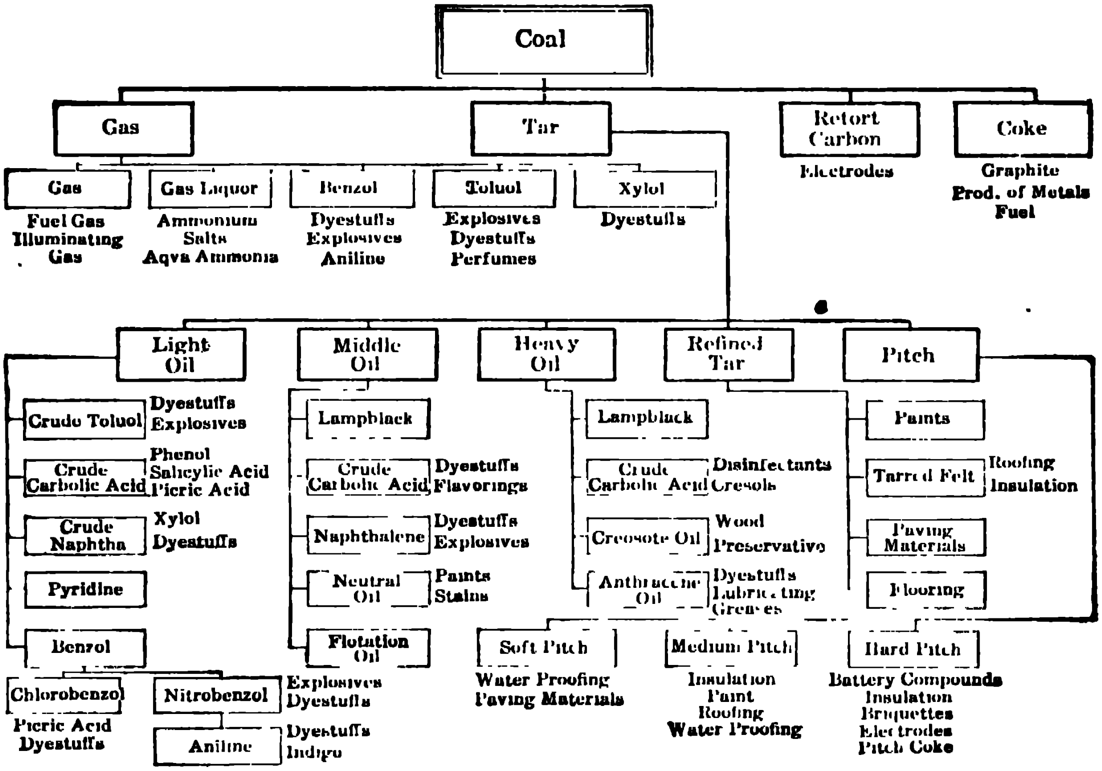
350. Asphalt, Bitumen.—The heavy, black, solid residue, left in the retort after the more volatile constituents of California or Mexican petroleum have been distilled off, is called *asphalt*. It consists of unsaturated hydrocarbons of high molecular weight, associated with oxygen-containing bodies of obscure character, and smaller quantities of compounds containing nitrogen and sulfur: Natural deposits are found in many parts of the world, notably as the famous Trinidad Lake containing several million tons, on an island off the coast of Venezuela. The material varies in composition and characteristics, according to its origin.

Trinidad asphalt is solid, and will not melt when thrown into boiling water. It is used for paving and roofing, and for making black varnishes and lacquers. Material of similar nature, of lower melting point, and perhaps semi-liquid at ordinary temperatures, is called *bitumen*, or mineral pitch. It has been used from the times of the Ancient Egyptians and Babylonians down to the present day, for caulking the seams of ships, for setting stones in courses of masonry, and for waterproofing wood.

351. Benzene, Toluene, and Xylene.—Modern coking ovens, for the production of metallurgical coke (§ 328) are often equipped with means for recovering not only ammonia but a number of other by-products. The gas from the retorts is first purified, as just described for domestic coal-gas. It is then passed upward through a series of steel towers (Fig. 90) filled with tile or brickwork, down which trickles a current of heavy fuel oil, carefully freed by distillation from all the volatile constituents of ordinary petroleum. This dissolves and removes from the gas the vapors of benzene and several other hydrocarbons (chiefly toluene and xylene), which are liquid at ordinary temperatures, but so volatile that they can be separated from the gaseous products of distillation only by the use of a solvent.

Benzene is now used in very large amounts in the manufacture of phenol (sometimes called "carbolic acid"). Benzene is also an important solvent for rubber, the solution being used for impregnating fabrics in the manufacture of waterproof clothing, and casings for automobile tires. It is often blended with gasoline, for use as a motor fuel. Benzene, toluene, and xylene are all used in the manufacture of explosives, dyes, drugs, perfumes, and photographic chemicals.

352. Coal-tar Products.—Coal-tar is a heavy, black, sticky fluid of unpleasant odor; but, in spite of its disagreeable qualities, it is one of the most useful substances known. From it are derived, directly or indirectly, a great number of brilliant dyes, valuable drugs, explosives, antiseptics, and perfumes. It gives us waterproof paints and enamels, phonograph records, automobile fuel, electrical insulation, wood preservatives, roofing, and roads.



353. Rubber.—Rubber (or caoutchouc) is a complex hydrocarbon, or mixture of hydrocarbons, of the formula $(C_5H_8)_n$. This indicates that its molecule is an unknown and probably variable multiple of the group C_5H_8. A simple hydrocarbon, **isoprene,** having the formula C_5H_8, is obtained by the destructive distillation of rubber; and rubber of an inferior sort has been made from isoprene.

Such a union of two or more identical simple molecules to form a more complex molecule is called **polymerization.** Rubber is thus often referred to as a **polymer** of isoprene. Although we know this much concerning the structure of the rubber molecule, its production from cheap materials, in duplication of the natural product, is one of the problems that organic chemistry has yet to solve.

Rubber is produced by several hundred species of plants, mostly natives of the tropics, though hardly more than half a dozen of these species are of any commercial importance. The world's consumption of rubber is above 300,000 tons a year, of which more than a third is worked up in the one city of Akron, Ohio. Rubber is drawn from the plant as a milky latex, which consists of a colloidal solution (§ 91) of rubber dispersed in a watery fluid. The colloidal particles seem to be covered over and stabilized by a coating of other material; but acetic acid, or the acrid smoke from a wood fire, causes the droplets of rubber to coagulate, or gather together in a curdy mass. The product is *crude rubber.* This is finely ground and washed with running water to remove impurities, then kneaded with one of the so-called fillers, the best of which are *lamp-black* and *zinc oxide.* These, and the kneading process itself, increase the toughness, hardness, and tensile strength of the rubber.

Pure rubber is sticky in warm weather, and almost as stiff as sheet iron when cold. To overcome these faults, and to enable it to remain pliable over a greater range of temperature, it is blended with sulfur, in a process called vulcanizing. For this, either sulfur itself is used (hot vulcanizing) or, less commonly, some compound which will slowly liberate sulfur in a finely divided condition. Vulcanization is assumed to consist, at least in part, in a chemical union of the sulfur with the unsaturated hydrocarbon molecule; but its exact nature is still unknown. Many substances are known which serve as *accelerators* of the vulcanizing process; zinc oxide has this property, in addition to serving as a filler. With the best of these accelerators, it is possible to vulcanize rubber at room temperature in a few hours' time. *Hard rubber* contains up to 30 per cent sulfur.

354. Essential Oils. Turpentine and Rosin.—Many plants produce oily liquids of aromatic odor, easily volatilized in a current of steam, and consisting of a mixture of organic substances, among which hydrocarbons are conspicuous. These are the **essential oils.** Examples are the oils of lemon and eucalyptus, as well as the perfumes distilled from the leaves and flowers of many plants.

The essential oils differ from the mineral oils, discussed at the beginning of this chapter, in consisting of unsaturated hydrocarbons (§ 310), intermingled with considerable quantities of substances (such as esters, § 361) which are not hydrocarbons at all; they differ from the edible fats and oils (§ 362) in not being convertible into soaps by boiling with alkalies.

The most important essential oil is **turpentine.** When purified by distillation in a current of steam (footnote, § 311), it consists largely of the hydrocarbon pinene, $C_{10}H_{16}$. The residue left behind, at the end of the distillation, is rosin, an impure organic acid of complex constitution. American turpentine is derived from the long-leaf pine of the Southern States.

Over 200,000 tons of turpentine each year are used—chiefly in admixture with linseed oil (§ 362)—as a constituent of paints. Turpentine owes its value to the fact that it dries slowly by oxidation, being converted into a glossy, solid film, which clings tightly to the painted surface. An interesting industry connected with turpentine depends on the fact that pinene, its chief chemical constituent, may be converted into synthetic perfumes (§ 374) and artificial camphor, identical in chemical composition with the natural products.

FIG. 90A.—An unexploited source of hydrocarbons. A view of a part of the enormous oil-shale deposits of Utah. The darker streaks are the richer beds. It is estimated that these deposits are capable of yielding forty billion barrels of oil, and half a billion tons of ammonium sulfate. But numerous problems concerning the mining and destructive distillation of this shale still need to be solved, while the difficulties to be met in refining shale-oil to produce acceptable motor fuel are likely to prove very serious.

EXERCISES

1. Illustrate the difference between an empirical formula and a structural formula.

2. What are isomers? Show that there are four isomeric hexanes, C_6H_{14}.

3. Write the structural formula of propane, and show that there are four different dichlor-propanes obtainable from it, according to the positions relative to each other of the two hydrogen atoms replaced by chlorine.

4. Does your state produce any petroleum? What are the prospects of future development? What is the chemical character of local petroleum, where is it refined, and what are the products of refining? (Reports of State Geologist, or references furnished by instructor.)

5. What are the three principal sources of motor fuel? What qualities other than heating value, in calories, need to be considered in the purchase of a motor fuel?

6. Draw up a chart or flow sheet (after the fashion of § 352) to show the principal operations in the refining and fractional distillation of petroleum, and the uses of the chief products.

7. Distinguish between hydrocarbons and carbohydrates (§ 365).

8. Calculate the relative weights of water and carbon dioxide produced by burning a fuel of the average composition, C_6H_{14}.

9. Write a brief report on the characteristics of the different types of coal (encyclopædia or chemical dictionaries). What are the characteristics of the nearest local deposits?

CHAPTER XXVI

ALCOHOLS, ORGANIC ACIDS, AND ESTERS

355. Alcohols.—An *alcohol* is an organic compound consisting of a *hydrocarbon radical* in combination with one or more *hydroxyl* groups (example, C_2H_5OH).

Methyl alcohol (methanol) or wood alcohol, CH_3OH, is obtained by the destructive distillation of wood. Recently, it has been synthesized very cheaply by direct union of carbon monoxide and hydrogen, in presence of a catalyzer (§ 76):

$$CO+2H_2=CH_3OH.$$

It is intensely poisonous, a very small quantity being sufficient to cause death or permanent blindness. It is used in the manufacture of formaldehyde, as a solvent in the preparation of varnishes, and for denaturing grain alcohol, and is the most promising future source of automotive fuel.

Ethyl alcohol (ethanol) or grain alcohol, C_2H_5OH, is one of the half dozen most useful organic substances; and, next to water, the most important solvent. It is made by the action of any one of a number of different microörganisms on sugar—a process called **fermentation.** But ethyl alcohol prepared in this way is always associated with small amounts of alcohols of higher molecular weight (for example, **propyl alcohol, C_3H_7OH; butyl alcohol, C_4H_9OH; amyl alcohol, $C_5H_{11}OH$**). These **higher alcohols** are oily liquids, collectively known as **fusel oil.** Several of them have recently become of great commercial importance, as solvents in the preparation of lacquers.

The most important higher alcohol is **normal butyl alcohol,** which is used in the preparation of normal butyl acetate, a valuable solvent (§ 361). Normal butyl alcohol is manufactured on a large scale by a fermentation process. Corn mash, carefully sterilized by heat, is inoculated with spores of **Weizmann bacteria,** which ferments starch directly to normal butyl alcohol and acetone. Air must be rigidly excluded, by carrying out the fermentation in deep vats or in the presence of hydrogen, and extreme precautions need to be taken to prevent foreign organisms from entering. To accomplish all this on a large scale has called for the development of methods that make this the world's outstanding example of Bacteriological Engineering—such interesting details as corn mash circulated through pipes previously sterilized by high-pressure steam; circulation pumps with pistons passing through loose packings wet with a solution of phenol (carbolic acid); and elaborate provisions for isolating a single spore of bacteria, and then propagating from this a pure culture sufficient to ferment the contents of a vat 20 feet in diameter and 20 feet deep.

Another useful higher alcohol is isopropyl alcohol, $(CH_3)_2CHOH$, which is synthesized from the propylene gas, C_3H_6, that results from the cracking of fuel oil in the manufacture of gasoline (§ 315). This is but one of a series of useful substances, other than hydrocarbons, which have recently been synthesized from petroleum. Research now under way promises rapid developments in new directions.

Another important alcohol is **glycerol** or glycerin, $C_3H_5(OH)_3$ (§§ 362, 363). This is obtained chiefly as a by-product in the manufacture of soap (§ 363); but it is interesting to note that glycerol has been produced commercially by fermentation of cane sugar. The fermentation is carried out in the presence of a strong solution of sodium acid sulfite, which prevents the growth of other organisms than the one responsible for the production of glycerol.

There is but one methyl alcohol, and one ethyl alcohol. But there are two different propyl alcohols, C_3H_7OH; four different butyl alcohols, C_4H_9OH; and larger numbers still of the following members of the series (not all found in fusel-oil). The explanation for the existence of so many isomers (§ 312) is to be found in the fact that the hydrocarbon radical may either be branched or unbranched; while the hydroxyl radical may be attached to any one of a number of different carbon atoms.

356. Production of Alcohol by Fermentation.—Alcohol (by which we always mean ethyl alcohol) may be prepared commercially from grain, fruits, tubers, cane or beet molasses—**in fact from almost any substance rich in starch or sugar.** Even **sawdust** may be hydrolyzed by acids, producing fermentable substances.

1. If the raw material is **starch** (grains or tubers) this must be converted into sugars before it can be fermented. The raw material is ground and heated with water to gelatinize the starch. The resulting " mash " is treated with **malt** (i.e., ground sprouted barley) which contains an enzyme (diastase, § 368) that enables the starch to enter into chemical union with water, forming fermentable sugars, glucose and maltose. Certain molds (*Mucor*) accomplish the same result (amylo process). Roughly formulated:

$$\underset{\text{Starch}}{3C_6H_{10}O_5}+2H_2O=\underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Maltose}}{C_{12}H_{22}O_{11}}.$$

When the material has thus been prepared for fermentation, it is brought to a proper temperature and yeast added. This unicellular plant is unable to make use of sunlight (photosynthesis, § 325) after the fashion of higher plants; but must derive the energy needed for its growth by the partial oxidation of sugar withdrawn from the surrounding solution. The chief products of this reaction are ethyl alcohol and carbon dioxide,

$$C_6H_{12}O_6=2C_2H_5OH+2CO_2;$$

but small quantities of the higher alcohols, glycerol, acids, and esters, are always produced.

2. If the raw material is **sugar** (from molasses) the preliminary treatment with dilute acid, malt, or mold is of course unnecessary. For though cane sugar and other sugars of the formula $C_{12}H_{22}O_{11}$ are not directly fermentable, still most strains of yeast secrete an enzyme (invertase) which slowly converts them into fermentable sugars of the formula $C_6H_{12}O_6$:

$$\underset{\substack{\text{Sucrose}\\ \text{(cane sugar)}}}{C_{12}H_{22}O_{11}+H_2O} = \underset{\substack{\text{Glucose}\\ \text{(grape sugar)}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ \text{(fruit sugar)}}}{C_6H_{12}O_6}.$$

Fermentation converts these two new sugars into alcohol and carbon dioxide.

In any case, the alcoholic liquor, at the end of the fermentation process, is run into huge cylindrical stills, and the alcohol distilled off with steam. This "crude spirit" is of course contaminated with the various esters and higher alcohols that have been mentioned as by-products of the fermentation process. In modern practice it is therefore subjected to an elaborate process of repeated fractional distillation, which results in practically pure ethyl alcohol, containing about 5 per cent of water.

357. Industrial Uses of Alcohol.—Alcohol for industrial use is commonly **denatured,** or rendered unfit for drinking, by addition of any one of a great many different substances. The best-known formula prescribes methyl alcohol, with a little kerosene or bone oil. Millions of gallons of alcohol are consumed each year as a **solvent** in the manufacture of smokeless powder, celluloid, photographic films, varnishes, and lacquers. Considerable quantities are also used as an **anti-freeze,** and as a raw material in the manufacture of ether, vinegar, chloroform, iodoform, and dyestuffs.

Alcohol has a smaller fuel value, pound for pound, than gasoline. But it burns more efficiently than the latter, and thus may actually furnish more miles to the gallon. In some parts of the world it is regularly used as a motor fuel, though automobile engines must be specially designed for its use, if it is to give maximum efficiency. A recent development is a commercial method for producing *absolute alcohol* (i.e., alcohol completely free from water). This may be blended with gasoline, to produce a fuel which burns without forming troublesome deposits of carbon.

358.—Ether and Acetone.—The substances called **ethers** may be regarded as **oxides of hydrocarbon radicals.** The most familiar compound of this group is **ethyl ether, $(C_2H_5)_2O$,** our most important surgical anesthetic, and a highly useful solvent. It is made by heating a mixture of ethyl alcohol and sulfuric acid to 120° C., in the presence of aluminum sulfate as a catalyzer The reaction takes place in two steps:

$$C_2H_5OH + H_2SO_4 \rightleftarrows \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{(C_2H_5)HSO_4} + HOH.$$

$$(C_2H_5)HSO_4 + C_2H_5OH = (C_2H_5)_2O\uparrow + H_2SO_4.$$

Acetone, $(CH_3)_2CO$, is produced by the destructive distillation of wood (or calcium acetate); and by the fermentation of starch (§ 355) in the absence of air. It is used as a solvent for acetylene, and for the extraction of gums and fats. A solution of cellulose acetate (§ 370) in acetone is used as a varnish for waterproofing airplane wings.

359. Chloroform and Iodoform.—When alcohol or acetone (§ 361) is treated with bleaching powder, a complicated set of reactions takes place, resulting in **chloroform, $CHCl_3$,** a volatile liquid of sweetish odor, which is **an important solvent and anesthetic.**

Iodoform, CHI_3, a familiar surgical antiseptic, is a yellow powder made by the electrolysis of a solution of sodium iodide, containing alcohol or acetone.

360. Organic Acids.—All organic acids contain one or more **carboxyl groups,—COOH.** They are the substances responsible for the sourness of certain fruits and vegetables. They react chemically with alcohols to form esters (§ 361).

Much acetic acid is produced by the destructive distillation of wood. The retorts or ovens are of sheet steel, heated externally, and connected to water-cooled condensers. Uncondensable gases consisting largely of methane and carbon monoxide, given off in large quantities, are burned as fuel under the retorts themselves. The condensed liquid is separated from the **wood-tar,** and neutralized with lime to form **crude calcium acetate.** This is recovered by evaporation and decomposed by sulfuric acid to form commercial acetic acid.

Enormous quantities of acetic acid are now produced from acetylene. This may be combined with water, in the presence of mercuric sulfate as a catalyzer, to form acetaldehyde, which may then be oxidized to acetic acid:

$$\underset{\text{Acetylene}}{C_2H_2}+H_2O=\underset{\text{Acetaldehyde}}{CH_3CHO}.$$

$$2CH_3CHO+O_2=\underset{\text{Acetic acid}}{2CH_3COOH}.$$

Since acetylene is derived from calcium carbide, which is produced from coke in an electric furnace, we have here an example of the synthesis of an important organic substance, directly from the element carbon. The last few years have furnished other examples of such methods, such as the synthesis of methanol from carbon, by way of carbon monoxide (§ 76), and the synthesis of tartaric acid from carbon, by way of carbon monoxide and sodium formate. Such synthetic methods, and such fermentation methods as that previously described for normal butyl alcohol (§ 355), are typical of the developments that are taking place to-day in industrial organic chemistry, and that seem destined to displace such wasteful and poorly controlled processes as the destructive distillation of wood.

Vinegar is a dilute acetic acid produced by the oxidation of ethyl alcohol under the influence of certain microorganisms:

$$\underset{\text{Ethyl alcohol}}{CH_3\cdot CH_2OH} + O_2 = \underset{\text{Acetic acid}}{CH_3COOH} + H_2O.$$

Since the process is one of oxidation, a plentiful supply of air is required. Dilute alcohol is permitted to trickle over chips or shavings, which have become covered with a growth of the acetic organism. Ordinary vinegar owes its flavor in part to other organic substances than acetic acid.

361. Esters.—**An *ester* is a substance formed by action of an acid on an alcohol.** Water is always produced at the same time:

$$H_2SO_4 + C_2H_5OH = \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulfate}}}{C_2H_5HSO_4} + H_2O;$$

$$CH_3COOH + C_2H_5OH = \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O.$$

The **simplest esters** are volatile liquids of pleasant odor, responsible for much of the fragrance of flowers, fruits, perfumes, and flavoring extracts.

Ethyl acetate, $CH_3COOC_2H_5$; amyl acetate, or "banana oil," $CH_3COOC_5H_{11}$; and normal butyl acetate of considerable importance in the manufacture of varnishes, lacquers, and imitation leather (§ 370).

An important artificial ester is *nitroglycerine*, chemically termed *glyceryl nitrate*, made by treating glycerol with a mixture of nitric and sulfuric acid:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O.$$

The sulfuric acid is for the purpose of absorbing the water that is liberated, thus preventing the reverse reaction. Nitroglycerine is a constituent of dynamite and smokeless powder. *Esters of cellulose* have many important uses to be described later (§ 370).

362. Vegetable and Animal Fats and Oils.—The esters of the greatest commercial value are the **vegetable and animal fats and oils**—such things as beef fat, lard, butter, olive oil, and linseed oil.

Some of these are important foods. Others serve as raw material for the manufacture of paints and varnishes, soap, and glycerol. The vegetable and animal fats and oils are esters, consisting of organic acids of high molecular weight, in combination with the one alcohol, glycerol, $C_3H_5(OH)_3$. For this reason they are often called **glycerides.**

If we let R represent a hydrocarbon radical, then the organic acids may be represented by the general formula $R \cdot COOH$; and the union of such an acid with glycerol, to form a glyceride may be formulated:

$$3R \cdot COOH + C_3H_5(OH)_3 = (R \cdot COO)_3 \cdot C_3H_5 + 3H_2O.$$

Some of the natural glycerides have actually been synthesized on a small scale by this reaction, the organic acid and glycerol being heated together in an autoclave, under pressure.

The reverse reaction—*hydrolysis of a glyceride to form glycerol and a fatty acid*—may generally be accomplished by boiling the glyceride with a dilute mineral acid (catalytic agent).

The vegetable and animal oils and fats range by imperceptible stages from fluid oils, through soft buttery solids, to waxlike solids. They have no true melting points, for they are all mixtures of different natural glycerides. Often, however, some one ingredient is of predominating importance. Thus beef tallow and butter consist largely of tristearin, the glyceride of stearic acid, a saturated compound (§ 310); while lard and cottonseed oil contain a noteworthy percentage of triolein, the glyceride of oleic acid, an unsaturated compound.

The oily, unsaturated glycerides, such as cottonseed oil, may be made to combine with hydrogen in the presence of finely divided nickel as a catalytic agent, and thereby become saturated, solid fats. This catalytic hydrogenation of oils is an important industry (§ 76).

The unsaturated glycerides unite directly not only with hydrogen and the halogens but with *ozone* and even *atmospheric oxygen.* In extreme cases, when spread out thin, an oil may, by absorbing oxygen from the air, be converted into an impervious, solid film (as happens with the hydrocarbon, turpentine). **Paint** is such a **drying oil,** mixed with a finely ground opaque pigment.

Varnish is usually a solution of rosin or some wax or wax-like substance in a mixture of drying oils. **Lacquer** may be similar to varnish, or it may be a solution of a resin or cellulose ester (§ 370) in a properly chosen solvent.

The new lacquers used on automobile bodies (such as Duco finish) contain gums, pigments, and a variety of cellulose nitrate capable of forming a solution of low viscosity. The solvent is a mixture of esters, hydrocarbons, and alcohols. When exposed to the action of sunlight or ultraviolet light, the cellulose nitrate loses oxides of nitrogen, and reverts to a modified form of cellulose. The outer layer of the dried lacquer thus gradually becomes insoluble in the very solvents used in applying it.

363. Soap and Soap-making.—The art of soap-making was known in the early days of the Roman Empire, as is witnessed by a soap factory which has been uncovered at Pompeii; and even savages, in various parts of the world make use of clays of a soapy quality as cleansing agents; or employ the bark of certain plants which have the property of forming a suds with water.

Soap-making is a process of decomposing vegetable and animal fats and oils by a caustic alkali (lye, § 44). The general formulation would be

$$\underset{\text{One molecule of fat}}{(R\cdot COO)_3C_3H_5}+3NaOH=\underset{\text{Three molecules of a soap}}{3R\cdot COONa}+\underset{\text{One molecule of glycerol}}{C_3H_5(OH)_3}.$$

Caustic potash (KOH) would serve as well (but produces soft soap). Thus **soap is a mixture of sodium (or potassium) salts of fatty acids.**

Soap is mostly made from the fats and oils that are rancid or of too inferior quality to be used as food. The sodium salt of rosin, a substance having acid properties (§ 354) is frequently mixed with the sodium salts of the true fatty acids, in the cheaper grades of laundry soaps. A modern soap kettle may hold several carloads. Dilute sodium hydroxide solution (12 per cent NaOH) is run in at the same time as the strained oil or melted tallow (soap-stock), admitting steam through the bottom of the kettle to keep the mixture well stirred. When the reaction seems to be over, the solution is carefully adjusted to leave no alkali in excess. Salt is then added, which causes the soap to separate to the top of the kettle as a solid curd. The solution containing the glycerol is drawn out at the bottom, concentrated by evaporation, and the glycerol recovered by evaporation in a vacuum.

364. Why Soap Cleanses.—Soap, in most cases, does not loosen and remove dirt by chemical action. This is evident from the fact that the substances removed may be of such utterly diverse sorts as clay, graphite, mineral oils, and saponifiable fats. If the substance to be removed is a film of oil, the rubbing breaks this up into minute droplets, which adsorb (§ 327) a film of soap and are thereby stabilized and prevented from reuniting.

A second effect—and the more important one, in the case of solid substances like graphite—is an alteration of the surface condition of the textile fiber and incrusting substance, resulting in a weakening of the force of adhesion. Particles which previously clung firmly to the fabric are made to transfer themselves to the surface films surrounding the air bubbles that make up the foam or suds. This effect is mainly due to the trace of alkali (NaOH) which is always present in a soap solution as the result of hydrolysis, since the fatty acids, as a group, are *inactive*. It is only occasionally that the alkali acts chemically by entering into direct union with substances of acidic nature, such as rosin or free fatty acid.

Dilute caustic soda is sometimes used in laundering, though it weakens most fabrics; and substances of faintly alkaline reaction, such as sodium carbonate or sodium silicate (water-glass) are common ingredients of washing powders or laundry soap. If such substances are used alone, one may secure an alteration of surface condition and consequent transfer of particles from fabric to foam; but will fail to secure the other effect, due to the action of soap in furthering the dispersion and removal of films of grease and oil.

EXERCISES

1. Describe the successive steps by which starch may be converted into ethyl alcohol, with equations.
2. What weight of glucose must be fermented to produce a liter of alcohol (sp. gr. 0.80), assuming the yield (§ 194) to be 90 per cent? What volume of CO_2 gas, at standard conditions, is liberated at the same time?
3. Mention four processes described in this chapter, in which microörganisms play a part.
4. How are the following substances prepared from ethyl alcohol: ethyl acetate, ether, chloroform, acetic acid?
5. Write structural formulas for ethyl alcohol, formic acid, ether.
6. What are the following, how produced, and for what used? Fusel oil, acetone, denatured alcohol, nitroglycerine, activated charcoal, benzene, benzine, naphtha, naphthalene, glycerol, amyl acetate, formalin, hydrogenated cottonseed oil?

7. Explain why linseed oil and turpentine are superior to naphtha as paint vehicles.

8. What are the following: Malt, maltose, diastase, glucose, fructose, petrolatum, methanol, iodoform, toluene, isoprene, boiled linseed oil, lacquer?

9. Given beef tallow, chiefly $(C_{17}H_{35}COO)_3C_3H_5$, how would you prepare soap? Write equation. How is soap thus produced separated from the other product of the reaction? How would you prepare stearic acid, $C_{17}H_{35}COOH$ (an insoluble compound), from this soap? Write equation.

10. Explain the difference in the chemical nature of mineral and vegetable oil.

11. By what simple test may a saturated hydrocarbon be distinguished from an unsaturated one? Illustrate by an equation.

12. To what group of organic substances does nitroglycerine belong? What method does this fact suggest for decomposing a quantity of nitroglycerine in order to render it harmless?

CHAPTER XXVII

SOME ORGANIC CHEMICAL INDUSTRIES

365. What Are Carbohydrates?—Carbohydrates are substances containing carbon in combination with hydrogen and oxygen, the last two elements being present in the same proportion as in water. Thus, starch and cellulose (wood fiber) have the empirical formula $C_6H_{10}O_5$—i.e., $C_6(H_2O)_5$—and cane sugar is $C_{12}H_{22}O_{11}$—i.e., $C_{12}(H_2O)_{11}$. But this is only a manner of speaking, for **it is impossible to cause carbon to unite directly with water to form carbohydrates.**

The simplest carbohydrates are called **sugars.** These are **crystalline, soluble compounds.** Several dozen different sugars are known. The more complex carbohydrates, many of them insoluble in water, are the **starches, inulins, gums, and celluloses** (wood fiber).

The colloidal, non-crystallizable nature of these substances makes them difficult to purify and separate from each other. We are thus ignorant concerning the number of different insoluble carbohydrates that exist in nature, and do not know whether specimens obtained from different kinds of plants are the same or different chemical individuals.

366. Sucrose and Invert Sugar.—We have just remarked that **the soluble crystallizable carbohydrates are called *sugars*.** These may contain as many as twenty-four carbon atoms in a molecule, or as few as two. But the most important sugars are those of the formulas $\mathbf{C_6H_{12}O_6}$ **(monoses)** and $\mathbf{C_{12}H_{22}O_{11}}$ **(bioses).**

Cane or beet sugar, or **sucrose,** one of several known sugars of the formula $C_{12}H_{22}O_{11}$, is obtained commercially from the sugar-cane and sugar beet, but is found in noteworthy quantities in the sap of the maple, sorghum, and many other plants, and in the juice of most fruits. We have already noted that sucrose is not directly fermentable to alcohol, but must first take up water and be changed into a mixture of glucose and fructose, through the action of an enzyme (*invertase*) contained in the yeast plant (§ 356). This same transformation can be brought about by other enzymes or by warming the cane sugar solution for a few minutes with a dilute acid:

$$\underset{\substack{\text{Sucrose}\\\text{(cane sugar)}}}{C_{12}H_{22}O_{11}}+H_2O=\underset{\substack{\text{Glucose}\\\text{(grape sugar)}}}{C_6H_{12}O_6}+\underset{\substack{\text{Fructose}\\\text{(fruit sugar)}}}{C_6H_{12}O_6}.$$

A solution of cane sugar rotates the plane of polarization of polarized light to the right (see text-books of Physics). But after the above change has taken place the direction of rotation is found to be reversed, or inverted. For this reason **a mixture of equal parts glucose and fructose is commonly called *invert sugar*,** and the process by which such a mixture is produced from sucrose—namely the addition of water under the influence of an enzyme or a dilute acid—is called **inversion.** Invert sugar is the principal constituent of honey; for the sucrose contained in the nectar of flowers is almost completely inverted in the honey-pouch of the bee, during its transportation to the hive. When honey crystallizes it is normally glucose that separates, for fructose is much the more soluble of the two sugars concerned.

In an industrial process recently developed, a rather concentrated cane sugar solution is partly inverted by a commercial preparation of invertase. The result is a sirup useful for canning fruit, which will not crystallize so readily as a solution of pure cane sugar.

An important difference between sucrose and the two constituents of invert sugar is observed when these are heated with *Fehling's solution.* This is a solution of cupric hydroxide in Rochelle salts (sodium-potassium tartrate, $NaKC_4H_4O_6$). Glucose and fructose both have pronounced *reducing properties;* and on boiling a solution of either of them with Fehling's solution, the copper is reduced from the cupric to the cuprous condition (forming a brick-red precipitate of cuprous oxide, Cu_2O) while the invert sugar is oxidized to a mixture of organic acids. Cane sugar has no effect on Fehling's solution, unless it is partly inverted by long boiling.

367. Sources and Uses of Sugar.—The world produces about 14,000,000 tons of sugar each year (1920) of which about 5,000,000 tons are consumed in the United States—almost 100 lbs. a year for each inhabitant. Though most of this is consumed as food, there are many other important uses. Sugar is a constituent of many kinds of shoe-blacking and printer's ink, and is often added to toilet soaps as a filler. About two-thirds the total production comes from the sugar cane, grown in the tropics and sub-tropics; and one-third from the sugar beet, grown mainly in the higher temperate latitudes: Nebraska, Colorado, Idaho, California, and Western Canada. Previous to the recent decrease in beet sugar production in Europe, cane and beet sugar were produced in about equal quantities.

The sugar beet contains about 15 per cent of sugar. The manufacture of beet sugar begins with a *diffusion battery*—a series of large vertical tanks, into which the sliced beets are placed, and extracted by warm water. The extraction is a process of dialysis (§ 380). The sugar and other crystallizable substances pass through the walls of the cells, and the mucilaginous or colloidal substances, of the nature of gums or albuminoids, remain behind.

But even after this preliminary purification, beet juice contains more foreign substances than juice expressed from cane. **It is found necessary to add a rather large excess of *lime*** (**or calcium saccharate**) **in order to coagulate and throw down the impurities. Then the excess of lime is removed as calcium carbonate, by adding *carbon dioxide* gas to the juice in several successive stages.** Sometimes sulfur dioxide gas is used to bleach the juice, alone or in combination with the carbon dioxide. The purified liquor is then concentrated to crystallization in vacuum-pans (Fig. 33) and the crystals of *raw beet sugar* separated by centrifuging.

A considerable additional amount of sugar is generally recovered from the beet sugar molasses by taking advantage of the fact that sucrose at about room temperature unites directly with lime to form a definite crystalline **calcium saccharate** (sucrate) of the formula $2CaO \cdot C_{12}H_{22}O_{11}$. This is used instead of lime in clarification of juice from the diffusion batteries. Sometimes strontia, SrO, is used instead of lime.

A good grade of white sugar is often produced directly from the cane, at modern cane-sugar plantations. But raw beet sugar has a slight soapy odor and taste, and needs to go through a special refining process.

368. Starch and Dextrin.—Starch $(C_6H_{10}O_5)_x$ is formed in the leaves of all green plants as a result of photosynthesis (§ 325) and is thence transferred and redeposited in tuber, seed, or stem. In the United States the principal source is corn (maize). The American corn crop commonly exceeds 75,000,000 tons a year, of which about 1,000,000 tons are used in the starch industry. Other sources of starch are **wheat, rice, cassava,** and the **potato.** The granules of starch from all these different origins are of different characteristic shapes and sizes, and readily identified under the microscope.

In the preparation of starch from corn, the grain is bleached and softened with a solution of sulfurous acid. Then it is coarsely grated, and the oily part of the seed separated by flotation and used as cattle food or for the preparation of corn oil, for soap making. The starch granules, by mechanical agitation with running water, are separated from the mucilaginous material, or gluten, with which they are associated. The dried product may amount to almost half the weight of the original corn.

Starch solutions are prepared by pouring cold starch paste into boiling water. This causes the granules to swell up and burst the thin covering of cellulose with which they are surrounded.

Solutions and pastes from different kinds of starch vary greatly in viscosity and adhesiveness. These properties may also be altered by addition of traces of alkali (thickening) or acid (thinning), thus modifying the material to suit its different applications ; as food, in laundrying, as an adhesive, and in the preparation of glucose sirup.

Since starch does not form true solutions in water, we are unable to get its molecular weight by freezing-point or boiling-point determinations. All we can say is that its formula must be some unknown multiple of the empirical formula $C_6H_{10}O_5$. By the action of diastase, an enzyme contained in malt (§ 356), starch is rapidly converted into maltose, which has the same formula as cane sugar, $C_{12}H_{22}O_{11}$. Dilute acids carry the process still further, giving glucose, $C_6H_{12}O_6$, as a final product.

When starch is cautiously heated it is converted into **dextrin,** a gum-like substance of faintly sweetish taste, fairly soluble in water, and used in enormous quantities as an adhesive, in coating postage stamps and envelopes. Dextrin is an important constituent of the crust of bread.

369. Glucose Sirup.—Thousands of tons of corn starch are now converted each year into **glucose sirup,** used as a table sirup and in the preparation of confectionery. In spite of its name, the principal constituent of glucose sirup (sometimes called commercial glucose or corn sirup) is not glucose at all, but **dextrin,** with smaller proportions of **maltose** and **glucose.** The idea is to have enough dextrin gum in the sirup to prevent the sucrose or glucose from crystallizing out of the confectionery in which the sirup is used; and enough maltose and glucose to give the mixture considerable sweetness, and thus spare cane-sugar.

The corn starch, carefully freed from nitrogenous impurities, is mixed with very dilute *hydrochloric acid*, and heated for about ten minutes in an autoclave, under a pressure of several atmospheres. The liquid is then neutralized with sodium carbonate, filtered, concentrated to a sirup by evaporation in a vacuum, then decolorized by bone-black, in much the same way as in sugar-refining.

370. The Cellulose Industries.—In cotton and linen fiber we have a carbohydrate called **cellulose,** of the same empirical formula as starch—$(C_6H_{10}O_5)_x$. Like starch, too, it may be hydrolyzed by dilute acids, though more slowly, yielding glucose. But cellulose occurs in fibers instead of in granules, is insoluble in boiling water, and is not stained by iodine.

The fibrous parts of growing young plants consist principally of cellulose, in a somewhat hydrated form. But as a plant develops its tissues harden, and may be converted into wood, which contains cellulose in association with **lignin,** a complex substance of variable composition, related to the carbohydrates, but having a decidedly lower proportion of oxygen. Most woods contain also noteworthy quantities of resinous material, coloring matter, and ash-producing substances.

1. Industries using fibrous material, in the natural or slightly altered form.

Many great industries make use of raw materials consisting largely of cellulose:

Lumber Textiles Mercerized fabric Paper (§ (§ 371).

In the textile industries, vegetable fibers are used in the largest quantity, and cotton leads all these. The United States furnishes about 1,500,000 tons each year, which is roughly two-thirds of the world's production. The bleaching of cotton goods has been described in § 162. When cotton is immersed in a strong solution of sodium hydroxide, the fibers swell up and lose their characteristic flattened and twisted structure. If it is then stretched, and thoroughly washed with cold water, to remove the excess of alkali, we have *mercerized cotton*, prized for its silk-like luster, and for the facility with which it may be dyed.

Linen is prepared from the stalk of the flax plant. To make good fiber the flax must be harvested before it blossoms, and very few districts produce both fiber and seed. The flax fiber carries a much larger proportion of gum and ligneous matter than does cotton, and must be purified and separated by a slow and troublesome process called *retting*, consisting in bacterial fermentation under water.

2. Industries using cellulose that has been partly or completely dissolved, then reprecipitated.

Vulcanized fiber Waterproof paper "Artificial" silk.

Vulcanized fiber is made by running paper through a solution of zinc chloride, which gives it a gelatinous coating of hydrated cellulose. It is then wound on rolls to form solid blocks. These are put through an elaborate washing process to remove the zinc salt, then pressed flat and dried. Vulcanized fiber is an important electrical insulator, as easily worked as wood, but harder, of a more uniform texture, and very nearly oil-proof.

"Artificial" silk is a lustrous form of cellulose, not chemically related to silk at all, and by no means so strong. The annual production now amounts to many thousand tons—in the United States, Europe, and Japan. Cellulose is dissolved in an appropriate solvent, and forced by air pressure through extremely fine openings in a perforated capsule (spinneret) into a precipitating bath of acid or alkali. The fibers are washed with dilute acid and water, and dried under tension in a current of warm air.

3. Industries depending on complete destruction of the cellulose molecule:

Destructive distillation of wood, producing methyl alcohol, acetone, acetic acid, and wood tar.

Ethyl alcohol from sawdust (hydrolysis by dilute sulfuric acid, followed by fermentation, § 356).

4. Industries using cellulose esters.

Smokeless powder Dynamite Celluloid
Lacquers Imitation leather Photographic films

Cellulose, like glycerol, has the properties of an alcohol and may accordingly (§ 364) be brought into combination with mineral or organic acids to form **esters.**

1. *Cellulose acetate.*—This is used in lacquers for metals, and for coating airplane wings or preparing imitation leather, artificial silk, and non-inflammable films.

2. *Cellulose Nitrates.* — When cotton is treated for a few moments with a slightly diluted mixture of nitric and sulfuric acids it is converted into a mixture of cellulose nitrates, commonly known as **soluble cotton, soluble nitro-cellulose, or pyroxylin,** which is used for making photographic films.

Pyroxylin dissolves in a mixture of alcohol and ether to form collodion. When heated and kneaded with camphor it forms *celluloid*, which can be moulded under pressure into an unlimited variety of forms—windows for automobile curtains, combs, brush-handles, and toys. Imitation leather, used for automobile tops, is canvas impregnated with a pyroxylin solution, or with pyroxylin and cellulose acetate, mixed with lampblack.

But when cotton is nitrated with a more concentrated mixture of acids, or when the mixture is allowed to act for a longer time, the reaction proceeds past the pyroxylin stage and we get a more highly nitrated product, no longer soluble in alcohol-ether. This is **guncotton, or insoluble nitro-cellulose:**

FIG. 91.—Nitrating cotton in the manufacture of photographic film.

$$\underset{\text{Cellulose}}{C_6H_7O_2(OH)_3}+3HNO_3=\underset{\text{Guncotton}}{C_6H_7O_2(NO_3)_3}+3HOH.$$

The sulfuric acid used serves merely to take up the water that is formed, thus rendering the reaction more complete.

Smokeless powder is made by mixing nitroglycerin (§ 431) with twice its own weight of guncotton, with some acetone as a solvent, and a little vaseline. The acetone evaporates, leaving the explosive mixture of nitrocellulose and nitroglycerin, as a horny mass (**cordite**). When such material explodes, the oxygen of the nitrate groups serves to oxidize the rest of the molecule, largely to CO_2 and water vapor, releasing most of the nitrogen in elementary form.

371. Paper.—The first step in the manufacture of paper consists in the preparation, by mechanical or chemical methods, of a pulp of finely divided fibers. This is then mixed with water and flowed on to a moving screen, which permits the water to drain away, and produces a mat or felt of wet fibers. This is dried and hardened into paper by pressing between rollers. The principle is very much like that by which hornets and wasps produced paper from macerated wood, long before man ever thought of such a substance.

The finest grades of paper are made from linen rags. These, are carefully selected, cleaned by boiling with dilute caustic soda, then passed through washing, cutting, and beating machines to reduce them to a fine pulp, which is usually bleached with chlorine. **Sizing** is anything added to the paper pulp to fill up the pores of the finished paper and keep the ink from spreading.

Commonly, the sizing consists of sodium resinate (rosin soap, § 367) and alum or aluminum sulfate. These two substances react, giving aluminum resinate and sodium sulfate. The aluminum resinate is then largely hydrolyzed into aluminum hydroxide and free rosin, which remain in the finished paper. Sizing also very commonly contains talc, China clay, and other finely divided white minerals.

Most of our paper is, however, made from spruce, and other kinds of wood. This is reduced to pulp by pressing the wooden blocks against revolving stones, cooled by running water. The cheapest grades of paper are made from this **mechanical wood pulp,** mixed with about one-third of its own weight of pulp which has been purified by chemical treatment. Newspapers are printed on such material, the most perishable literature of the day being thus very fittingly consigned to the poorest grade of paper.

Chemical wood pulp is made by reducing the wood to fine chips, from which the resin and lignin are then removed by digesting under pressure with various reagents.

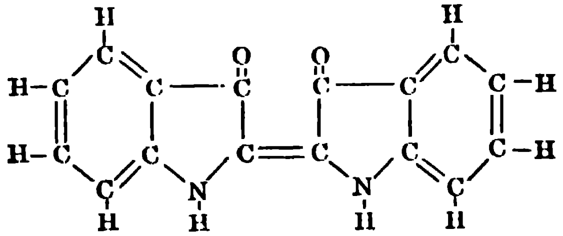
Sometimes a dilute solution of sodium hydroxide is used, or an alkaline solution of sodium sulfate (Kraft paper). But in the process most in use, the chips are digested under pressure in huge tile-lined cookers, with a solution of calcium acid sulfite, made by passing an excess of sulfur dioxide into a suspension of calcium hydroxide. A single cooker may hold as much as 50 tons of chips. After digesting for a number of hours, the extracted chips are reduced to a pulp, which is washed, screened, bleached, and finally incorporated with sizing, according to the kind of paper to be made.

372. Colored Substances and Dyestuffs.—Colored substances appear colored because they absorb certain special wave-lengths from the mixture that constitutes white light, reflecting or transmitting all other wave-lengths. Thus, blood absorbs wave-lengths corresponding to the green part of the solar spectrum, and transmits a mixture of other rays that give us the sensation that we call red.

Many substances that appear colorless to the eye do actually absorb light in the invisible part of the spectrum, beyond the violet (ultra-violet); others absorb the invisible infra-red light at the other end of the spectrum. Thus there are but few substances, if any, that ought strictly to be termed colorless. They merely *appear* colorless because human vision can perceive only a fraction of the spectrum that may be surveyed with a camera.

Many substances that appear to the eye to be intensely colored would never be useful as dyes. **To serve as a dye, a substance must not only be colored but must cling so firmly to fabric that hot water and soap fail to break up the combination.** This quality is lacking in most colored organic substances. **When the colored substance, however, contains a group that gives it acid or basic properties it is very commonly serviceable as a dye.**

From prehistoric times until the middle of the last century most of the coloring matters used in dyeing cloth were natural products. Examples were cochineal and lac dye from insects; and madder, turmeric, logwood, and indigo, from plants. But in 1856, Perkin, an Englishman, discovered a violet dye called **mauve,** the first of the numerous modern synthetic dyes, prepared from the substances obtained from the fractional distillation of coal tar (§ 352)—whence the designation **coal tar dyes.** Numerous investigators, in the years following Perkin's discovery, were engaged in synthesizing new dyes and in working out the formulas of those already known in nature. One of the first achievements was the synthesis of **alizarin** (the basis of **Turkey red**)—a dyestuff formerly prepared from madder root. Then, in 1881, **indigo** was synthesized, though twenty years of research and the expenditure of several hundred thousand dollars in cash were necessary before its manufacture (from naphthalene) was well developed, and an undoubted commercial success.



Structural formula of indigo

At the present time these synthetic dyes have largely replaced the natural products, and thousands of acres formerly devoted to the cultivation of indigo and madder are available for foodstuffs. The synthetic dyestuffs are purer and of more uniform quality than those produced in nature. Several thousand of them are now known, suited to all kinds of fabrics, and of every imaginable hue. Of synthetic indigo alone, the United States is said to consume more than ten million pounds a year.

When an acid or basic dye is used on silk or wool, it unites with the fiber directly, without the assistance of any third substance. This is called **direct, or substantive, dyeing.** The material to be dyed is simply steeped in a solution of the dye—commonly made acid with acetic or sulfuric acid, to release the color acid from the salt which constitutes the commercial dye. Sometimes the solution is heated, and the goods plunged in again, to secure a more intense shade. It is presumed that the silk or wool is slightly hydrolyzed during the heating, under the influence of the sulfuric acid in the dye bath. Basic and acid groups, in the silk or wool, previously combined with each other, are thus released for combination with the dye.

Mercerized cotton (§ 370) or cellulose nitrate and acetate (§ 370) dye directly, like silk and wool. But though there are a few dyes that dye cotton and linen directly, in most cases these fibers need first to be steeped in a solution of a **mordant**—a substance which becomes fixed in the fiber in an insoluble form, and then unites with the dye. A few dyes even require the assistance of a mordant in order to dye silk or wool. Ths most important mordants for the acid dyes are readily hydrolyzable salts (acetates, chlorides, and sulfates of aluminum, chromium, iron, copper and tin, § 113).

373. Chemistry in Medicine.—Among primitive peoples and in ancient times, the practice of medicine was in the hands of magicians and priests. With no scientific principles to guide them, they administered almost every imaginable substance as a medicine, very often with fatal results. But among countless failures, these early practitioners of the healing art now and then scored a success, discovering by pure accident some natural substance capable of exerting a well-marked physiological action, or possessed of real curative properties.

Thus it was discovered that an extract of the bark of the cinchona tree, found in Peru, will cure malaria; that a preparation from the juice of the poppy induces sleep; and that certain plants produced poisonous substances, which served as stimulants when administered in small doses. Various inorganic medicaments—preparations of arsenic, antimony, and mercury—were introduced during the Middle Ages. Then, within the last century, came the discovery of general anesthesia by nitrous oxide, chloroform, or ether, and the use of numerous inorganic and organic substances as germicides and antiseptics.

But medical chemistry, to this very day, has remained in a primitive state in two important particulars:

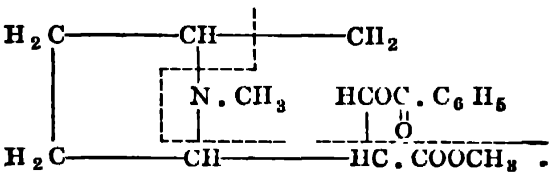
1. **The medicinal substances found in nature have been employed very largely as they happen to occur, without any special attempts at purification.** The chemical compounds responsible for their useful properties have often remained unknown; and the preparations that have been administered have been of uncertain strength and potency, and have often contained unknown amounts of ingredients of an actually harmful nature.

2. **Such chemical substances as have been employed in medicine in a pure form were first prepared with quite other ends in view.** Their physiological actions were often brought to light by merest chance, long after chemists had been familiar with their more obvious properties. Ether, for example, has been known since the thirteenth century, but its anesthetic properties were noted for the first time in 1846. Again, almost a quarter of a century elapsed after the discovery of amyl nitrite before it was found that this substance gave almost instant relief from the agonies of angina pectoris. Ethylene, C_2H_4, recently hailed as a new anesthetic, with such valuable properties that it may displace the rest, was actually discovered in 1795.

With the rapid development of organic chemistry, however, in the half century just closed, came the isolation of a large number of the pure compounds of definite medicinal properties from the crude drugs of former days: cocaine, a soluble, white, crystalline compound, from the leaves of a South American plant (*Erythroxylon coca*); strychnine and brucine, from the seeds of the strychnos bean; morphine, from opium; quinine and cinchonine, from Peruvian cinchona bark; atropine from nightshade. The examples here listed all happen to be **alkaloids**—nitrogenous substances of complex constitution, having the property of uniting directly with acids to form crystalline salts.

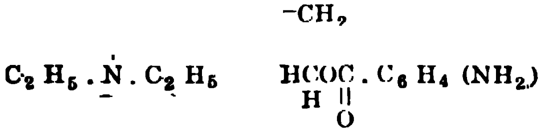
Furthermore, within the past few years, medico-chemical research has entered upon a new stage of development: the attempt to discover whether the physiological effect obtained with a given compound may not be due to some particular small group of atoms within its molecule—perhaps best obtainable from some near relative of the given substance.

Take the case of cocaine, which has been used for many years as a local anesthetic, in dentistry and minor surgical operations. Laborious research has proved it to have the structural formula,

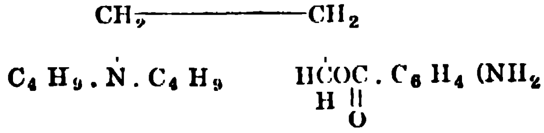


As soon as this information had been gained, physiological chemists set to work to synthesize new compounds having molecules built upon architectural plans resembling that of cocaine, but with modifications. Thus it was presently discovered that only the portion of the cocaine molecule that is marked with a star—above and to the right of the dotted line in the preceding formula—is responsible for its capacity for deadening pain. The rest of the molecule is worse than useless, for it contains groups that relate the substance to nicotine and poison hemlock.

The result is that cocaine is rapidly being displaced by synthetic alkaloids, quite unknown in nature, with molecules "cut to measure" Examples are—



Procaine



Butyn

A glance will show that these substances contain the groups specified above as necessary to a local anesthetic of this type, and very little else. These products, and a number of other closely related synthetic alkaloids, are safer than cocaine, because less poisonous. Furthermore, they are more stable toward heat, and therefore more easily sterilized.

374. Synthetic Perfumes and Flavors.—The use of perfumes and flavors dates from prehistoric times, and their production at present is a larger industry than most persons would imagine. The world—or the feminine half of it—is now thought to consume at least two thousand tons of perfume each year, for which it pays many million dollars.

Many fruits and flowers owe their odor to simple aliphatic or aromatic esters Examples are amyl acetate, or banana oil, and methyl salicylate, or oil of wintergreen. But oil of turpentine, and the oils of the citrus fruits, consist largely of aromatic hydrocarbons—members of what is called the terpene series. Others, again, are largely aldehydes, ketones, or phenols, with smaller quantities of compounds containing sulfur or nitrogen.

The natural perfumes call for so much labor in collecting the blossoms from which they are obtained, and require such care during the process of extraction, that their price is necessarily very high. The organic chemist has accordingly entered this field, seeking first to identify the compounds responsible for the odor of the natural perfumes, and then to synthesize them from cheaper materials. Here the patient labor of the research chemists of two generations has at last won the same degree of success as in the synthesis of dyes and medicinal substances.

The artificial duplication of any of these odors involves, first, the separation of the natural material into its several constituents; second, the working out of the structural formula or plan of architecture of the molecules of the substances thus isolated; third, the synthesis of these substances from easily available raw material; fourth, the blending of the odoriferous substances thus produced to duplicate the natural perfume. The second and third steps are, of course, the most difficult and often call for years of expensive research. But even the final blending may prove a most vexatious problem, for many perfumes owe much of their distinctive odor to substances contained in them in traces too minute for identification.

Nevertheless, many natural flavors and perfumes have already had to yield much of the field to their synthetic duplicates. Essences of lilac and lily of the valley are now made in ton lots, from turpentine; essence of violet from lemon oil; vanilla from oil of cloves; while blends in imitation of the elusive odors of the rose and heliotrope, together with fragrant mixtures never known in nature, are produced in large quantities.

375. Organic Chemistry and the National Welfare.—The industries based on synthetic organic chemistry are of special importance to the nation as an element of military preparedness and economic independence. The chemical industries are a means of defense more effective than would now be afforded by an impregnable fortified frontier, or an absolute command of the seas. For the chemical substances of military importance are derived from the same sources as those employed in peace, and involve similar steps in their preparation. A factory making fuchsine dyes from phosgene (§) is in a position to deliver, on a few hours' notice, quantities of this toxic gas for filling shell. One making synthetic phenol for manufacture of synthetic resin (bakelite) can very easily turn its product into a high explosive (picric acid). Photographic developers, lacquers and varnishes, drugs and anesthetics—all these products of chemical industry in the organic field must be produced in vastly increased quantities, in times of military activity. If the world must experience another war, the country lacking ample facilities for the manufacture of organic chemicals of the most diversified sorts may well tremble for its safety.

In the end, however, an economic policy must be justified by something more than the fear that science may again be put to the unspeakable uses of a few years ago. One may doubt whether the happiness and welfare of the people of a nation at large are increased by the too-zealous exploitation of foreign markets, especially of those for unmanufactured raw materials; but, concerning the advantages to a country of being self-sufficient in such industries as demand highly trained hands and brains, opinions can hardly differ. The nation can ill afford to let any industry languish that puts a premium on intellect.

England, France, and Japan have taken measures to protect their vital organic chemical industries by protective tariffs, or absolute embargoes. In the United States, such legislation is made difficult by the fear of creating a "dyestuff monopoly," and a definite policy of protection awaits the development of favorable popular opinion.

Fig. 92.—Inspecting the finished nitrocellulose product—a sheet of photographic film.

EXERCISES

1. How many milligrams of invert sugar are present in each cubic centimeter of a solution prepared by inverting 3.42 g. of sucrose, and diluting the solution to 1 liter?

2. How is each of the following prepared, and what chemical compounds does each contain? Glucose sirup, mercerized cotton, vulcanized fiber, rayon, pyroxylin, celluloid.

3. What weights of carbon dioxide and water are produced by the complete combustion of 1 g. of pure cellulose? What volume will this carbon dioxide occupy, at standard conditions?

4. What is the source and chemical nature of rosin? Representing rosin by HR, give equations to show how it is applied in sizing paper.

5. What volume of sulfur dioxide gas, at standard conditions, is required for every kilogram of quicklime, in preparing calcium acid sulfite, for paper making?

6. Cite two reactions to illustrate the fact that cellulose has the chemical properties of an alcohol.

7. Ethylene, C_2H_4, is prepared by passing the vapor of ethyl alcohol through a heated tube containing clay balls, which serve as a catalyzer. The process is one of dehydration. Write equation, and determine what volume of ethylene, at standard conditions, can be produced from 1 g. of alcohol.

8. Ethylene, mixed with nitrous oxide and oxygen, has recently been used in anesthesia. What is the percentage by weight of each of these three gases in a mixture in which they are present in equal proportions by volume?

9. Sketch a Bunsen flame in vertical section, and explain what happens in each zone. Why does a Bunsen flame, when receiving an insufficient supply of air, become luminous?

10. Distinguish between direct and indirect dyeing. What is a mordant? Write an equation to explain what happens when cupric acetate is used as a mordant.

11. Describe the method by which the percentage composition of most organic substances has been determined (analysis by combustion).

CHAPTER XXVIII

THE COLLOIDAL STATE OF MATTER

376. Crystalloids and Colloids.—Review § 94. When pure substances of simple chemical composition and low molecular weight are dissolved, we commonly obtain a true solution. Such substances are often referred to as **crystalloids;** examples are the inorganic electrolytes (acids, bases, and salts) and such organic substances as glucose, cane sugar, and urea. Substances of complex composition or high molecular weight, on the other hand, are often referred to as **colloids;** for they commonly form colloidal solutions when dispersed in a solvent. Examples are cellulose, rubber, the vegetable gums, starch, and albumen (white of egg).

The distinction between crystalloids and colloids is, nevertheless very indefinite. **In all probability, all substances may be made to assume the colloidal state.** Ice is commonly regarded as a crystalloid; yet we may obtain a colloidal solution of ice in chloroform by saturating the latter with water, then suddenly cooling it in a freezing mixture. The particles of ice thus formed are so small that they remain in suspension in the chloroform indefinitely; yet they are large enough to give the liquid a slightly milky appearance. Common salt and many other inorganic substances, *ordinarily seen in crystalline form, may also be obtained in colloidal* solution if they are produced by chemical reactions in the midst of organic liquids in which they happen to be insoluble. Conversely, many substances commonly regarded as colloids, such as egg albumen, may be obtained in crystalline form, if proper precautions are observed.

Accordingly, **a colloid is not a substance of a particular *chemical class*, but rather one having a tendency to assume a particular *physical state*—**a state in which it is subdivided to form particles of an extremely small size, which are dispersed or scattered through a second material. An automobile tire consists largely of colloidal particles of lampblack and various inorganic "fillers," dispersed in vulcanized rubber; and paint, of colloidal particles of pigment, dispersed in a drying oil (§ 554).

377. Colloids and Life.—To realize the overwhelming importance of colloids, one need but pause to consider that **all the phenomena of life are connected with processes that take place only in colloidal matter.** A seed is planted in the ground, and straightway there begins a contest for water, between seed and soil. In this contest, the seed wins, draws water into itself, and swells up until the seed-coat bursts. Here is a process that could never take place with crystalline material.

Presently growth begins. Little by little the stores of colloidal foodstuffs in the seed—starch, proteins, and fatty substances—are acted upon by enzymes, themselves of colloidal nature. Thus these reserves of food are converted into sugar and other crystalline material, transported in this form to growing stem or rootlet, and there rebuilt into colloid form. Soon the young shoot bursts from the soil, and unfolds its leaves in the sunlight. We then behold a new marvel—photosynthesis—the building up of starch, a complex colloidal material, from two simple crystalloids, water and carbon dioxide. Thus the plant grows, becomes a tree, and after many years brings forth fruit after its kind. Roots, trunk, branches, leaves, bark, and fruit all consist of colloidal substances, with nowhere any other crystalloid than water, if we except a few simple substances, such as sugar and organic acids, which form no necessary part of the plant, but merely represent material in transport or storage, and destined in proper time to be itself elaborated into colloidal living tissue.

Nor are plants alone thus intimately related to the *properties* of colloids. Every individual animal is built up from complex material called protoplasm, which contains many different chemical substances, and assumes many different forms. But whether this protoplasm belongs to amoeba or to man, it is essentially colloidal. **Large deposits of inorganic crystalloids are found in the animal body only in a few highly specialized structures, such as the bones and teeth** (and are even there in intimate association with colloids). Mineral salts also play an important part in regulating the water-holding capacity of organized colloids.

With these exceptions, it is as true of animals as it is of plants that crystalloids represent material held in reserve for future building operations or surprised in transport. If a living plant or animal were represented by a large city, then the different houses and office structures would represent the different kinds of colloidal material that compose the plant or animal. Crystalloids would be represented only by stocks of steel, lumber, brick, and stone, laid up in warehouses and storage yards; or by occasional truckloads of these materials that pass through the streets, on the way to locations at which new buildings are being erected or old ones remodeled or repaired.

378. Disperse Systems.— We have just referred to a colloidal solution as consisting of one kind of material dispersed in another. The material which is dispersed or subdivided is often referred to as the **disperse phase** * or **inner phase;** that through which the disperse phase is scattered is the **dispersion medium** or **outer phase.**

The different classes of disperse systems are often all illustrated at the dinner table:

Chinaware or porcelain. . . .	an opaque *solid* dispersed in a semi-transparent *solid* (§ 489)
Food served "steaming hot"	a *liquid* (droplets of water) dispersed in a *gas* (air)
Biscuits or cake .	a *gas* dispersed in a *solid*
Whipped cream	a *gas* dispersed in a *liquid*
Mayonnaise dressing, milk, butter, or jelly	a *liquid* dispersed in a *liquid* (an **emulsion**)
Chocolate.	a *solid*, dispersed in a *liquid* (a **suspension**)
Cheese.	a *liquid* (butter fat) dispersed in a *solid* (casein)
The smoke from a cigar. . . .	a *solid*, dispersed in a *gas* (air)

It is true that these are not all to be considered as colloidal systems, since the individual particles of the disperse phase, in several instances, are visible with a microscope, if not with the naked eye; but we have here all the different classes of disperse systems from which colloidal systems arise by continuing the process of dispersion until the dispersed particles become of less than microscopic dimensions, while still remaining large in comparison with molecules. **Coarse disperse systems pass over into colloidal solutions, and these in turn into true solutions, by imperceptible gradations.**

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* In chemistry, the word **phase** refers to a homogeneous portion of matter, separated by definite bounding surfaces from the other kinds of matter with which it may be associated. A mixture of sand and salt, in contact with a saturated salt solution, half filling a closed bottle, represents four phases: two solid, one liquid (solution), and one vapor.

Colloidal systems consisting of solid or liquid colloidal particles dispersed in a liquid dispersion medium are frequently called **sols.** If the dispersion medium is water, they are **hydrosols.** Examples are a colloidal solution of glue in water, and India ink.

379. The Two Classes of Colloidal Solutions.—If we saturate water with arsenious oxide, As_2O_3, and pass in a little hydrogen sulfide gas, we get a yellow colloidal solution of arsenious sulfide, As_2S_3. This may be kept for a long time if the water in which the arsenious sulfide particles are dispersed is very pure. Still, the slightest traces of acids, bases, or salts (collectively termed electrolytes, § 250) cause the colloidal particles to gather together in clusters, presently forming a visible yellow precipitate.

Many other colloids (but not all others) are easily precipitated by electrolytes. This is presumed to indicate that many colloidal particles carry electrical charges, and are precipitated when these are neutralized by other charges of opposite sign (furnished by the ions of the electrolyte).

Many familiar phenomena may be explained by the action of electrolytes on colloidal solutions. Farmers often apply finely ground limestone to heavy soils, not so much because the soils lack the calcium necessary for the growth of plants, but rather because the limestone is slightly soluble, producing ions in sufficient concentration to coagulate the clay, and render the soil more easily tilled. The same thing, on a gigantic scale, is witnessed at the mouths of the Mississippi, Ganges, Euphrates, and Nile. Colloidal material brought down by these muddy streams is deposited in the deltas, partly because of the sluggish movement of the water there, but chiefly because of the coagulating action of the salt of the ocean, that is mingled with the river water with every sweep of the tides.

A colloidal solution of glue (a hydrophilic colloid, § 94) is in remarkable contrast to one of arsenious sulfide. The colloidal particles of glue contain a large percentage of absorbed solvent (in this case water). This is often expressed by stating that they are **highly solvated.** They can be coagulated and precipitated only by adding a very large amount of a salt. Moreover, a glue solution is highly viscous, and becomes more viscous with decreasing temperature, finally setting to a stiff jelly; but a colloidal solution of arsenious sulfide will not form a jelly, no matter how concentrated it is made.

Colloidal solutions accordingly fall into two groups: a colloidal arsenious sulfide solution is an example of a ***suspensoid*****—a non-viscous, non-gelatinizing colloidal solution, easily coagulated by electrolytes, and containing colloidal particles but slightly solvated, with electrical charges definitely positive or negative.**

A glue solution is an example of an ***emulsoid*****—a viscous, gelatinizing colloidal solution, not easily coagulated by electrolytes, and containing highly solvated, liquid or semi-liquid particles, with no electrical charges at all, or with variable and irregular charges.**

It is interesting to notice that a *suspensoid* precipitated by an electrolyte cannot usually be redissolved. But when an *emulsoid*, such as albumen, is thrown down (as by a concentrated solution of ammonium sulfate) it will usually redissolve if placed back in pure water and washed free from adsorbed electrolytes. Colloids are accordingly sometimes classified as irreversible and reversible. Even a precipitated gold suspensoid can, nevertheless, be redissolved by dilute ammonia; while precipitated emulsoids, on the other hand (albumen), often undergo subtle changes on standing, which prevent them from being redissolved when treated with water.

380. Ultrafiltration and Dialysis.—Colloidal particles are so small that they pass through the pores of ordinary filter paper. It is nevertheless possible to separate them from their dispersion medium by means of an **ultrafilter.** This consists of a layer of jelly on some kind of supporting material, such as porous porcelain, or even filter paper. If a pressure of six to twenty atmospheres is applied, the dispersion medium may be forced through the jelly, but the colloidal particles remain behind. Thus we may demonstrate that dextrin, soluble starch, and certain dyestuffs really form colloidal solutions when they dissolve in water, though such solutions are perfectly clear and transparent and contain very few particles visible under the ultramicroscope. Recently ultrafiltration has been put to considerable practical use in studying enzymes and bacterial toxins, and in removing colloidal coloring matter from solutions of organic crystalloids. By the use of a suitably constructed ultrafilter, ordinary water may be rendered absolutely sterile.

The fact that jellies can act as finely-pored filters proves them to have a sponge-like structure (§ 381). By using jellies of different materials (gelatin, collodion, silicic acid) solidified from solutions of different concentrations, ultrafilters of different degrees of porosity may be obtained. Thus, colloidal particles of different sizes may be separated from each other. Some ultrafilters recently prepared appear to have pores not more than a dozen times molecular dimensions. Perhaps the end is not yet. If we had a straw fine enough—and patience enough—we might sip fresh water from a glass of brine.

We have mentioned the fact that the molecules of heavy gases, such as carbon dioxide, move with comparative slowness at any given temperature, and therefore diffuse very slowly through porous walls (§ 25). Colloidal particles, being very large in comparison with molecules, are still more sluggish, and diffuse very slowly indeed. We may accordingly determine whether a colored substance dissolves to form a true or a colloidal solution by pouring some of the solution over a colorless jelly, and noting whether the dissolved particles diffuse into the latter and stain it.

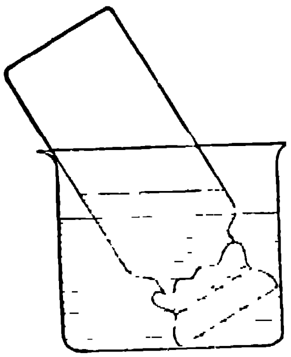


Fig. 93—Dialysis.

Another method for demonstrating the extremely slow rate of diffusion of colloidal particles is shown in Fig. 93. A solution containing both starch (a colloid) and common salt (a crystalloid) is placed in a widemouthed bottle, which is closed tightly with a sheet of parchment paper and inverted in a beaker of water. After a few minutes, some of the salt will have diffused through the parchment and the water outside the bottle will give a test for chlorides. But if the parchment membrane has been tied on tightly enough to prevent leaks, no starch will get through it for many hours, and the addition of a drop of iodine solution to the outer liquid will give no blue color. Such a separation of crystalloids from colloids, by diffusion of the former through a membrane, is called **dialysis.** It is of great practical importance in the purification of colloidal materials of all kinds.

The separation of colloids from crystalloids by dialysis is usually ascribed to the slower rate of diffusion of the former. But the fact that many of the membranes used in dialysis may be employed also in ultrafiltration suggests that in many cases the colloidal particles are really too large to get through the pores of the dialyzing membrane, even if they had a rate of diffusion comparable with that of crystalloids. Another noteworthy observation is that it is sometimes possible to separate crystalloids from crystalloids by means of a membrane. Thus, if a solution containing both sulfur and silver nitrate dissolved in pyridine is separated from pure pyridine by a rubber membrane, the sulfur passes through, and the silver nitrate stays behind. In such cases it appears that the crystalloid passing through is first *dissolved* in the membrane, and then handed on to the liquid outside.

381. Protective Colloids.—The typical emulsoid sols are commonly very stable, and not very easily precipitated by electrolytes. Accordingly, the addition of a very small quantity of an emulsoid, such as glue, to a suspensoid sol, tends to coat over and protect the suspensoid particles, and make them less easily precipitable. It is important to notice that the properties of a suspensoid which has been thus stabilized are almost completely masked by those of the protective emulsoid which it has adsorbed. Thus, the particles of metallic sols (such as a colloidal solution of gold) are in general positively charged; but when they adsorb glue they become electrically neutral, or have a variable and irregular charge.

Many important applications of protective colloids are made in the industries. A small amount of gelatine or calcium saccharate is always added to commercial ice cream. This helps to keep the material smooth by preventing the growth of crystals. Gum arabic in marshmallows serves a similar purpose. Gelatine in ice cream furthermore aids digestion by preventing the separation of the fats and coagulation of the milk in heavy curds. For the same reason, the addition of a small amount of gelatine or cereal gruel to cow's milk intended for infants or invalids will render it more digestible. Human milk carries a larger proportion of a natural protective colloid, lactalbumin, than does cow's milk.

India ink is a colloidal solution of lampblack, stabilized with gum arabic. Colloidal lubricants and fuels are now stabilized with tannin or rosin soaps. In photography, the plate or film consists of an emulsion of silver bromide with gelatin as a protective colloid. It is essential that the silver salt should remain finely grained. Very commonly, glue is added to the chemical mixtures used to treat boiler water for preventing boiler scale. It presumably acts by coating the precipitated particles, thus preventing them from adhering to the boiler tubes.

382. Gels.- Figure 94 illustrates what is believed to happen when an emulsoid sets to a jelly. At the left (*A*) we have a fluid sol, consisting of concentrated droplets of disperse phase scattered through a dilute solution constituting

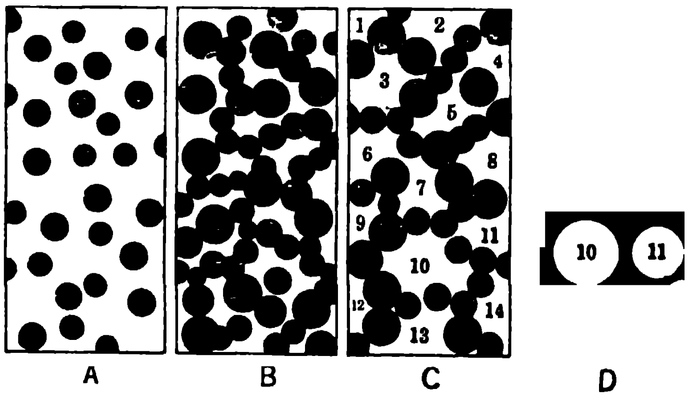


FIG 94 —Four stages in the formation of a gel.

the dispersion medium. The effect of cooling such a sol is to disturb the equilibrium between the droplets and the surrounding dilute solution. We infer that they draw more water into themselves, and increase in size, and perhaps come into contact (as shown at *B*) like cells of a honeycomb. Such a change would result in a very great decrease of fluidity--for if one should attempt to force such a mixture through a fine tube, the droplets would find considerable difficulty in rolling past each other.

By imperceptible stages—as the temperature is lowered or the dispersion medium is removed by evaporation—the sol loses its fluidity and assumes the half-rigid condition of a jelly, technically called a *gel*. Sometimes the term gel is applied as well to a gelatinous precipitate, such as aluminum hydroxide.

There is no definite temperature at which a gelatinization takes place, in the same sense that there is a definite temperature at which water freezes. For practical purposes, the temperature of gelatinization is taken as that at which the liquid becomes so viscous that it will no longer flow out when a test-tube containing it is inverted. But a certain amount of time is required for the setting to take place, which will be less the lower the temperature.

If the colloidal solution is a very concentrated one, there is reason for believing that further changes may take place. Thus, the droplets that constitute the disperse phase may coalesce and form viscous threads, leaving spaces between filled with relatively fluid dispersion medium. We have two interlacing phases, and the disperse system has a sponge-like structure (*C*). In extreme cases, the viscous particles or threads may unite to form a continuous phase, inclosing droplets of what was previously the dispersion medium (as shown at *D*). The structure of the original emulsoid sol is thus completely reversed: the more concentrated phase now acts as the dispersion medium, and the more dilute phase is discontinuous.

An interesting speculation—though at present little more than a speculation—is that living organisms transfer food material from cell to cell by an arrangement of this kind. A cell wall may at one moment be permeable to water and water-soluble substances, but impermeable to lipoids (substances of a fatty nature, § 387). Then some substance appears which, like Ali Baba at the cave of the Forty Thieves, is possessed of the magic word. The wall structure is reversed, the lipoid passes through, and immediately the gates swing shut.

383. Peptization.—The reverse of coagulation or precipitation (**pectization**) is the reduction of colloidal particles to a higher degree of dispersion by the addition of some foreign material. This process is known as **peptization.** There are occasions when a very large excess of an electrolyte will have this effect, thus reversing the usual precipitating action of such materials. Common examples are afforded by certain metallic hydroxides, such as those of chromium and aluminum, which are precipitated from solution by the addition of a small amount of sodium hydroxide, but appear to be redissolved by the addition of a further amount (§ 473).

A similar process is used commercially in preparing colloidal solutions of casein (the principal nitrogenous constituent of milk). The dry material is almost unaffected by water, but swells very rapidly when a small amount of some alkaline solution is present, and on further addition of water is peptized to form a viscous colloidal solution. This process finds many important commercial applications in the manufacture of adhesives, plastic materials, and paper sizing. In dissolving gelatine (glue) in water, the solvent itself acts as a peptizing material.

384. Electrical Transference of Colloids (Cataphoresis).—Suspensoid particles always carry electric charges, positive or negative. These may be as much as fifty or sixty times those carried by a univalent ion in a dilute electrolyte. The mass of each suspensoid particle is, however, very great, even in sols of the highest degree of dispersion, and the electrical resistance of colloidal solutions is correspondingly high. A high voltage will nevertheless force a current through, and with the apparatus of Fig. 94*a* the migration of the suspensoid particles under the influence of the electrical potential may easily be shown.

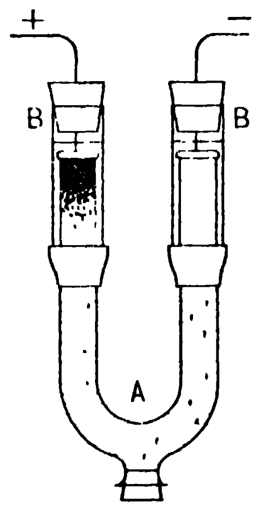


FIG. 94*a*.—Cataphoresis.

The ends of a U-tube (*A*) are covered with parchment paper or goldbeater's skin. It is then inverted, filled through the opening at the bottom with colloidal arsenious sulfide solution, and slightly stoppered. Finally, wide glass tubes (*B*, *B*) held in place by rubber bands, are slipped over the ends of the U-tube. After these have been filled with dilute acetic acid, and platinum or graphite electrodes inserted, the apparatus is connected with a

110-volt direct-current circuit. After half an hour the solution in the U-tube presents the appearance shown in the figure. Most of the suspensoid particles have migrated away from the neighborhood of the cathode (−), leaving that part of the liquid clear. The liquid around the anode (+) has in consequence acquired a deeper shade of yellow than before.

This experiment shows very clearly that the particles of colloidal arsenious sulfide carry negative charges of electricity. In fact, *most kinds of suspensoid particles are negatively charged.* But the particles in colloidal solutions of the metals and metallic hydroxides are usually positively charged.

385.—Mutual Precipitation of Suspensoids.—If a small amount of a solution of colloidal arsenic sulfide is added to a solution of colloidal ferric hydroxide, mutual precipitation takes place, and the two colloids are thrown down together. It is presumed that the negative charge of the arsenic sulfide particles has neutralized the positive charge of the colloidal ferric hydroxide particles; and suspensoids which precipitate each other almost always carry electrical charges of opposite sign. However, if a very large excess of either of the two colloids is used, the charge of the other one may be reversed, and no precipitation may take place. Thus, a very large excess of arsenic sulfide, added all at once to a limited quantity of ferrric hydroxide, will not produce precipitation.

EXERCISES

1. Define and illustrate: suspensoid, emulsoid, sol, phase, disperse phase, dispersion medium, gel, ultrafilter, cataphoresis.

2. Distinguish between osmosis and dialysis.

3. Tell how a colloidal solution of arsenic trisulfide is prepared Write equation. Explain why this solution cannot be prepared by passing hydrogen sulfide into a solution of arsenic trichloride (note the other product of the reaction and the effect that it would have on the colloidal arsenic sulfide).

4. Explain how colloidal solutions are purified, and how stabilized.

5. Be prepared to discuss the general methods for preparing colloidal solutions, as tabulated in the appendix.

6. Describe the Tyndall test for colloidal particles (§ 94). What is the principle of the ultramicroscope?

7. The Tyndall effect depends on difference in refracting power of the colloidal particles as compared with that of the dispersion medium Would you expect it to be most pronounced for suspensoids or emulsoids, and why? (Compare degree of solvation)

8. What is adsorption? Name several useful applications. How does it apply to the precipitation of suspensoids by electrolytes?

9. Describe a diffusion test to determine whether a certain colored substance dissolves to form a true or a colloidal solution

10 Tell what is presumed to happen in the formation of a gel. Which class of colloidal solutions forms gels?

11 Name two inorganic gels (§ 105, 471) Explain the nature of the difficulty met in giving such a substance a definite chemical formula How may such gels be peptized?

12. What substance is commonly used to stabilize each of the following colloidal systems: Mayonnaise dressing, kerosene-water emulsion, silver bromide emulsions (§ 515), India ink?

13. What is cataphoresis? Would you expect it to be most pronounced with suspensoid or emulsoid particles? Why?

14 A process that separates clay, by cataphoresis, from impurities consisting of small amounts of ferric and manganese hydroxides has met with some commercial success. What do you infer concerning the charge (+ or −) of colloidal clay particles?

15. Clay suspensions that are to be poured into plaster-of-Paris molds in the manufacture of pottery (§ 487) become more fluid in the presence of a small amount of alkali Explain

16. Can you point out some analogies between the phenomena accompanying the cleansing of fabrics with soap (§ 364)and those met in the concentration of an ore by froth-flotation (§ 361)?

CHAPTER XXIX

A GLIMPSE OF THE CHEMISTRY OF NUTRITION

It is now very nearly a century since the first of the great host of organic substances known to the chemists of to-day was synthesized by artificial means, without the aid of living plants and animals (§ 336). In the intervening years the science of organic chemistry has developed at a rate which an age marked by tremendous scientific advances of all kinds could hardly parallel. The theory that the molecules of organic substances are composed of individual atoms, arranged according to definite and discoverable plans, proved a safe guide for hundreds of researches, which won the most brilliant results. As intellectual achievements, indeed, the most noteworthy mechanical inventions of the century just closed—such things as the automobile, airplane, and linotype machine—can hardly be compared with the synthesis of the complex molecules of indigo, camphor, and the medicinal alkaloids. The mechanic works with materials that he can measure and lay out with compass, square, and gauge; while the chemist must create his masterpiece from fragments too small for human senses, and can take note of the progress of his work only with the inner eye of the mind, as he adds atom to atom.

These tremendous discoveries in the field of organic chemistry resulted not alone in the creation of great industries rivaling or surpassing Nature in the creation of useful products, but afforded, year by year, a better understanding of the manner in which Nature herself works. A century ago all the processes involved in the digestion and assimilation of foods were complete mysteries, and the subject of the wildest speculations. To-day, we know, in a general way, what happens when foods are digested. The simplest of the chemical transformations that take place in nutrition are, indeed, so well understood that we can duplicate them in beakers and test-tubes. Progress is still very rapid in spite of many difficulties that surround experimental work with living animals and human beings. Biochemistry, in fact, is already very highly specialized. We can here offer no more than a glimpse of a few of the most important facts that have been discovered concerning the chemical changes that take place when foods are transformed into living tissue.

386. Digestion and Absorption of Carbohydrates.—The chief functions of food are (1) to furnish **energy** for carrying out the vital processes; (2) to furnish **raw material for the building or rebuilding of tissue**; (3) to furnish **substances necessary for the proper stimulation or control of vital processes.**

Not all foods are equally valuable for these different purposes: carbohydrates and fats are preëminent as sources of energy;

proteins (§ 388) as tissue builders; mineral salts and unidentified organic substances (vitamines) as vital regulators. Yet it must be understood that there is no very strict division of duty among the different types of foodstuffs, for each, in its own special field, is supplemented and assisted by the others.

Of these three classes of foods, let us consider the carbohydrates first, since the soluble members of this group (the sugars) are the simplest of all organic foods, and the easiest to digest. Glucose and fructose are directly absorbed by the intestinal walls and enter the blood-stream unchanged. Sucrose is first inverted (§ 366) by the hydrochloric acid of the stomach and by an enzyme (§ 52) called **invertase,** present in the fluids secreted by the intestinal glands:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

Milk sugar or lactose, also having the formula $C_{12}H_{22}O_{11}$, is broken up in the same way into glucose, $C_6H_{12}O_6$, and **galactose,** $C_6H_{12}O_6$. The latter sugar, in combination with nitrogenous raw material, is a constituent of the brain and nervous tissue. This is perhaps the reason why milk sugar forms a part of the natural diet of young mammals.

Starch and dextrin (§ 368) are readily converted to maltose by an enzyme called **ptyalin,** present in the saliva:

$$\underset{\substack{\text{Starch or}\\ \text{dextrin}}}{2C_6H_{10}O_5} + H_2O = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}.$$

This process, begun during mastication, continues for a time in the upper end of the stomach, where the digestive fluid is neutral or slightly alkaline. It is finished just after the food is discharged from the stomach, by the **pancreatic diastase** of the pancreatic juice. Finally, the maltose is hydrolyzed to glucose by a third enzyme, **maltase,** of the intestinal juices:

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

The simple sugars (glucose, fructose, and galactose) produced by the processes just mentioned, are absorbed by the intestinal walls and enter the blood stream. Glucose, indeed, is everywhere present in the general circulation, to the amount of about 0.1 per cent; but any *excess* of glucose, and perhaps all the fructose absorbed from digested food, is converted into **glycogen**—or animal starch, $(C_6H_{10}O_5)_x$, a white powder soluble in water, which is stored up in the liver and in muscular tissue in all parts of the body—a reserve supply of carbohydrate.

Over half the energy needed by the body to maintain its temperature and to do muscular work comes from the oxidation of the glucose of the blood, in a succession of stages not yet fully worked out, to carbon dioxide and water:

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 677{,}200 \text{ calories.}$$

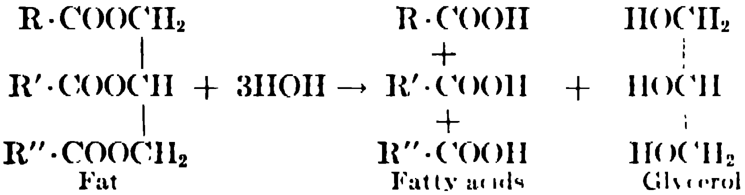
The total energy thus obtained by the body is the same as the heat energy that would be liberated by burning the same amount of glucose in a calorimeter. The carbon dioxide accumulating in the venous blood is eliminated through the lungs; and the glucose withdrawn from the arterial blood is immediately replaced from the stores of glycogen in liver and muscles. **Carbohydrate material digested and absorbed in excess of the actual energy requirements of the body will first produce glycogen; but if the excess supply is kept up, a deposit of fat will be formed.**

387. Digestion and Absorption of Fats.– The edible fats and oils are esters formed by combination of fatty acids with glycerol (equation in § 362).

Closely related to the fats are the **lipoids,** in which one of the three acid radicals is that of phosphoric acid, in combination with a nitrogenous organic base. An example is **lecithin,** the principal constituent of yolk of egg. The lipoids are essential constituents of nervous tissue, and are intermediate in their properties between the highly hydrated proteins and the anhydrous fats. Thus, living tissue, by virtue of its content of lipoids, is able to absorb and retain considerable quantities of water, without being dissolved.

The first step in the digestion of fats takes place in the lower (pylorus) end of the stomach. Here, by action of the stomach juices, combined with vigorous churning movement, the fats are broken up into minute droplets, which are dispersed to form a milky emulsion or colloidal solution. Thus, a physical condition is obtained that favors the ensuing chemical alteration, brought to pass in the small intestine, under the action of a fat-splitting enzyme, **lipase,** secreted by the pancreatic juice.

This chemical change is a simple hydrolysis, the fat being resolved into fatty acid and glycerol:



$$\begin{array}{cccccc} \mathrm{R{\cdot}COOCH_2} & & & \mathrm{R{\cdot}COOH} & & \mathrm{HOCH_2} \\ | & & & + & & | \\ \mathrm{R'{\cdot}COOCH} & + & \mathrm{3HOH} \rightarrow & \mathrm{R'{\cdot}COOH} & + & \mathrm{HOCH} \\ | & & & + & & | \\ \mathrm{R''{\cdot}COOCH_2} & & & \mathrm{R''{\cdot}COOH} & & \mathrm{HOCH_2} \\ \text{Fat} & & & \text{Fatty acids} & & \text{Glycerol} \end{array}$$

Both the products of this reaction appear to be absorbed by the intestinal wall, and are there resynthesized into fat, which is poured directly into the blood stream. When large quantities of a digestible fat are taken with the food, a part of this may retain its original chemical composition after entering the circulation, or even after being laid down in the tissues. Thus, sesame oil fed to a cow may appear unchanged in her milk and butter; and beef tallow produced by animals fed on cottonseed meal often has some of the chemical characteristics of cottonseed oil.

If given more time, however, the digestible fats are worked over and chemically altered. Radicals of certain acids may be split off and replaced by others. Further quantities of fat may be formed from carbohydrates. Thus every species of animal tends to produce its own characteristic kind of fat, regardless of the food on which it subsists.

388. Proteins.—Living tissue is composed largely of **proteins.** These contain carbon, hydrogen, and oxygen—the three elements present in the fats and carbohydrates—with nitrogen, and a very small amount of sulfur. A few proteins (conspicuously the **phosphoproteins,** contained in the brain and nervous tissue) contain phosphorus in addition. Proteins make up most of the solid matter of lean meat, as well as the glutenous (horny) portion of corn and other grains. A group of protein-like substances, called **keratins,** particularly rich in sulfur, are the principal constituents of horn and hair.

The proteins are white powders, of very complicated structure, very few of which are crystallizable. The true proteins, like many other colloids, absorb water readily, and in some cases are dispersed by it to form colloidal solutions. The water-soluble proteins are called **albumens.** Other proteins are peptized (§ 383) by dilute salt solutions, or by cold, dilute acids and alkalies. Most of the proteins contain about 16 per cent nitrogen, namely, about 1 part nitrogen to 6.25 protein. The protein in foods is thus often roughly estimated by determining the percentage of nitrogen and multiplying that by 6.25.

When proteins are digested, or boiled with dilute acids, they are decomposed, forming substances of simpler structure. The ultimate products of this process, which is really one of hydrolysis (§ 113), are the **amino acids.** These are crystalline substances, which may be considered as being derived from ordinary non-nitrogenous organic acids by replacing one or more hydrogen atoms by **amino groups,** $-NH_2$, or closely related nitrogenous groups.

Examples of amino acids are:

$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} \qquad \underset{\text{Tyrosine}}{C_6H_4OH \cdot CH_2OH(NH_2) \cdot COOH,}$$

$$\underset{\text{Alanine}}{CH_3 \cdot CH(NH_2) \cdot COOH} \qquad \underset{\text{Tryptophane}}{(C_8H_7N) \cdot CH_2 \cdot COOH.}$$

Altogether, about two dozen different amino acids are known.

The digestion of the proteins begins in the stomach, where they are hydrolyzed under the influence of **pepsin.** An interesting thing about this enzyme is that it is active only in the presence of a trace of hydrochloric acid, secreted by the glands of the intestinal walls.

The process of hydrolysis, begun in the stomach, is completed in the intestine, under the influence of other enzymes. These are in marked contrast to pepsin, in that they are most active only in faintly alkaline media.

The digestion of the proteins, in the successive stages just mentioned, results in amino acids. These are absorbed directly by the intestinal walls, carried by the blood stream to different parts of the body, and absorbed by the muscular tissue. Here they are worked over and rebuilt into living protein. Finally, as the living protein is broken down, during vital activity or muscular work, it passes again through the stage of amino acids, which yield up their nitrogen in the form of ammonia, to be excreted at last as urea.

389. Energy Requirements of the Body.—The total quantity of food that a human being or an animal needs to consume is determined largely by the amount of energy that it needs to obtain from that food. The food serves as fuel, being oxidized within the body, just as coal is burned under a boiler, liberating energy in the form of heat.

It is a matter of great practical importance, then, in the economical use of food, to determine what the actual energy requirements of the body are, in the different forms of rest or bodily activity. There are four different methods for doing this:

1. **By determining the total weight and kind of food consumed during a period of many weeks by individuals eating just sufficient food to maintain a constant body weight, while performing work of a definite kind.** The energy value of this food can be determined by burning samples of it in a calorimeter (§ 332); for it has been shown that the same amount of heat (for fats and carbohydrates) is thus set free as if the food were digested and oxidized within the body, forming carbon dioxide and water.

2. **By determining the quantity of oxygen consumed and carbon dioxide exhaled, in respiration, during a definite period.** The quotient, volume of carbon dioxide exhaled to volume of oxygen consumed, is called the **respiratory quotient.** When carbohydrates are burned in a calorimeter or oxidized within the body, the volume of carbon dioxide produced is equal to that of the oxygen consumed, or the respiratory quotient is 1:

$$C_6H_{12}O_6+6O_2=6CO_2+6H_2O.$$

For the oxidation of fats and proteins, which require relatively more oxygen, the respiratory quotient is lower—about 0.7. A respiratory quotient of 0.85 on a low-protein diet would indicate that fat carbon and carbohydrate carbon were being oxidized within the body in about equal quantities.

Analysis of inhaled and exhaled air accordingly gives us an indication of the kind and quantities of fuel that are being oxidized within the body, after making allowance for the protein oxidized, as measured by the urea excreted. Knowing the weights of the three principal food constituents, and the fuel value of each, one may make an estimate of the total energy requirements of the body, for the kind of bodily activity studied.

3. **By measuring the quantity of heat given off by the body, when a person is confined for a few hours in a small room with heat-insulated walls.** Such a room is called a **respiration calorimeter.**

4. **By calculation from the weights and chemical analyses of the foods consumed in a definite short period, as compared with the weights and analyses of excreta and exhaled air.** This method assumes that the amount of carbohydrate in the body remains constant during the experimental period, and that any increase or decrease in carbon or nitrogen stored in the body during the experimental period represents fat and protein.

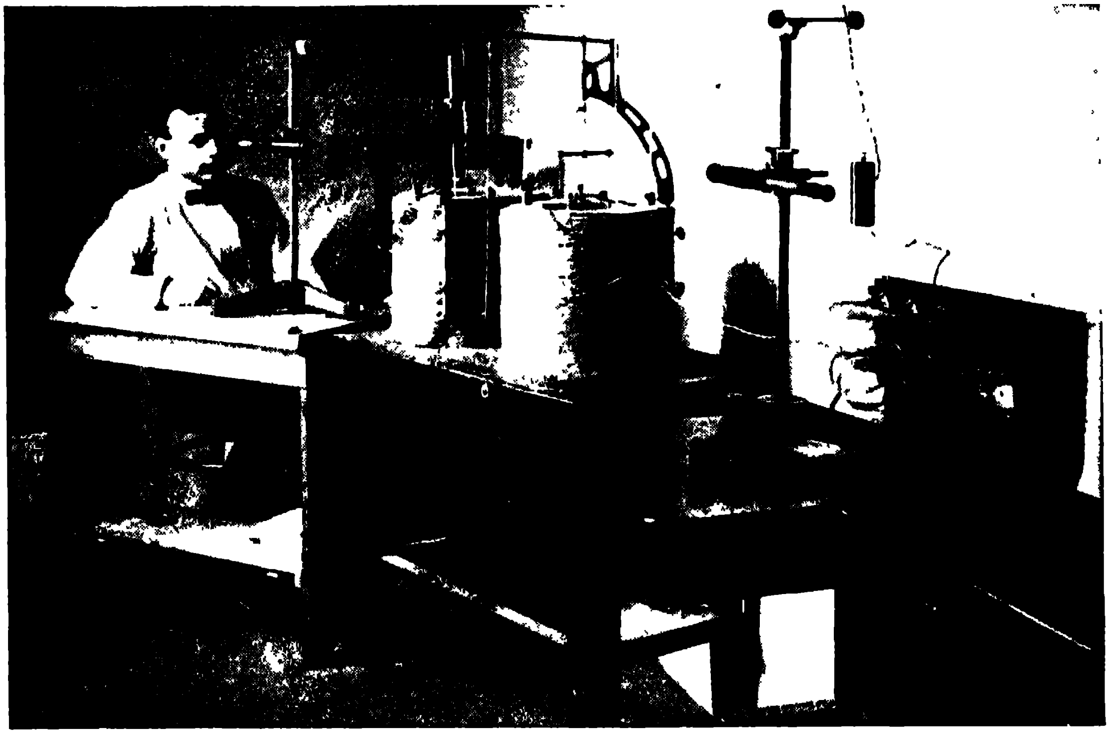


FIG. 95—Determining the heating value of coal by burning a sample in a calorimeter (see p 292). The rise of the thermometer is observed through a telescope The energy value of foods may be determined in the same way

These four different methods are in very good agreement. They show, for example, that a man of average weight (154 lbs.) requires about 85 large calories (85,000 small calories) an hour, when lying at complete rest, without taking food. This energy is expended within the body in the work of respiration, circulation, and other vital functions, and is liberated as heat. But the mere act of standing, or the work of digestion after meals, will add to this rate of expenditure of energy; and severe exercise will increase it several fold.

Now, as to the amount of food that one would need to consume, in order to obtain the amount of energy that is calculated as proper for one day, we ought to note that, so far as any one now knows, energy is energy, regardless of its source. Disregarding the complications that would come from an attempt to exist upon a single kind of food, the body may obtain energy to keep the blood in circulation, digest food, or carry on any other bodily function, from any one of the digestible and oxidizable constituents of food.

Foods rich in fat and poor in water have a much larger energy value than those poor in fat and rich in water. Thus, an ounce of olive oil is as good a source of energy as three pounds of cabbage. In any case, the percentages of protein, carbohydrates, and fat in a food (Appendix) will enable one to calculate the amount of energy one might reasonably expect to get by consuming a given weight of it.

390. Protein Requirements of the Body.—Though the energy requirements of the body, when performing various kinds of work, are fairly accurately known, there is difficulty in establishing the measure of its needs for protein. An adult person in good health is ordinarily in a condition of **nitrogen equilibrium,** proteins being digested and assimilated each day in quantity just sufficient to replace the nitrogen excreted through the kidneys in the form of urea. If the protein in the daily food is now increased, more nitrogen will be assimilated than before; but within a few days a new condition of equilibrium will result, in which the increased assimilation of nitrogen is balanced by increased excretion. This will commonly happen before the body has laid up any considerably increased store of nitrogen.

The minimum daily requirements of the body for nitrogen cannot be estimated from the nitrogen (or urea) excreted from the kidneys during fasting. For the body under such conditions makes an effort to conserve nitrogen, and for a short time probably excretes less of that element than it could continue to do indefinitely; while during the later stages of starvation, when the body has consumed its reserves of carbohydrate and fat, it is forced to burn protein instead, and the excretion of nitrogen is very much increased.

Accordingly, it would seem that the question of the actual needs of the body for nitrogen is best studied by observing what quantity of protein has been consumed, on the average, by persons existing for a long time on a low protein diet, but in nitrogen equilibrium, and in apparently excellent health and vitality. This average sufficient protein diet is about 50 grams of protein a day. Allowing a 50 per cent excess as a "factor of safety"—to insure a stock of mobile or reserve protein in the tissues, to be drawn upon in emergencies—we find that **a sufficient protein ration for an adult man, of average weight, is about 75 g. of protein each day.** This is contained in about—

		With a fuel value of about	
(*A*)	0 8 lb. dried beans.	1,200	large calories
	0 9 lb. lean beef sirloin (edible portion)	980	" "
	1 8 lbs. bread (white, average).	2,100	" "
	1 7 lbs. cheese (American pale).	1,100	" "
	5 pints milk..	1,600	" "
	1 lb. oatmeal.	1,900	" "
	11 eggs (average).	800	" "
(*B*)	7½ lbs potatoes (peeled, raw)	2,800	" "
	2 lbs rice	3,300	" "
	17 lbs. butter	58,000	" "

This table makes it very evident that certain foods (Group *A*) are so rich in protein that *too much protein* will be included if a diet, limited to these foods alone, is made of sufficient quantity to supply one's needs for energy (2500 to 3500 large calories). Of other foods (Group *B*) some have so high a fuel value that *too much energy* may be available if they are taken in sufficient quantity to furnish the proper supply of protein. A properly balanced ration must therefore include foods of both classes; but a further discussion must be postponed to (§ 393).

391. The Ash Constituents of Food.—Fifteen elements are known to be essential to the growth of the body. Of these, the three most plentiful in amount (O, C, H) are present in the fats and carbohydrates; two others (N, S) are present in the simple proteins as well. The remaining ten (five non-metals P, Cl, I, F, SI; five metals Ca, K, Na, Mg, Fe) are contained in food and in the body itself, in part in organic and in part in inorganic form.

Thus, when we refer to these ten elements (and S) as the **inorganic constituents of food,** we are merely using a manner of speech to distinguish them from the elements (O, C, H) most abundantly present in the bodily structure; and we do not mean to imply that they are not built into true organic compounds during the processes of metabolism. Phosphorus, for example, occurs in the body in inorganic form, as the calcium phosphate of the bones, as well as in the phospho-proteins, and in the fat-like substances called lipoids (§ 387). Sometimes these eleven elements are referred to as **the ash constituents of the body,** for they are always pretty largely retained in the ash that is left behind when such material is burned, whatever may have been the nature of the compounds in which they were originally present. It is fortunately true that whenever enough food is taken to satisfy the needs of the body for energy and protein, the ash constituents are usually supplied automatically in sufficient quantity. With phosphorus, calcium, and iron, however, there is some danger of running short.

An adult person is apparently safe if provided with 1.5 g. of **phosphorus** a day. This quantity of the element is to be obtained with certainty only by taking care that foods rich in phosphorus (milk, beans, whole wheat, oatmeal) form a sufficient part of the diet; and there is the further question, not yet entirely settled, whether phosphorus of inorganic salts is quite so valuable a nutrient, especially for growing children, as that contained in organic forms of combination.

Among the five metallic elements we find **calcium** the most plentiful. In combination with phosphorus, as calcium phosphate, it forms most of the mineral matter of the bones- in fact over three-fourths of the ash constituents of the body. But equally important is the function of the calcium salts contained in the blood, in promoting its coagulation when a vein or artery is cut. Calcium and sodium salts, furthermore, have a regulating influence on the action of the heart. Heart muscle, immersed in a solution of blood ash, will continue to beat for a long time, outside the body.

But in spite of the great importance of calcium in the metabolism, it is the element most likely to be insufficiently supplied in ordinary diets. A sufficient quantity of calcium for an adult person is believed to be about 0.7 g. a day; though several times that amount may be required during rapid growth. Meat happens to be very deficient in calcium. The most practical means of securing an abundance of calcium in the diet is to make liberal use of foods that contain it in conspicuous amounts (cabbage, turnips, milk, cheese).

Iron is of great importance as an essential constituent of the red coloring matter (*haemoglobin*) of the blood. In this form it serves as a carrier of oxygen, enabling the oxidizable constituents of the tissues and blood-stream to be oxidized, with the release of energy. Numerous experiments seem to show that the iron of haemoglobin can be derived only from the iron present in the foods in organic forms of combination. Such organic compounds of iron are found conspicuously in green vegetables and in eggs. These should form a part of the diet if danger of iron starvation is to be avoided. A few milligrams (15–20) of organic iron are probably sufficient for the average man. Women and children require relatively more, in proportion to their weight.

392. Vitamines.– The vitamines, a group of substances of little known nature, are needed in traces for normal growth. They are present especially in dairy products and green vegetables. The evidence for the existence and nutritive importance of the vitamines is entirely indirect. It has long been noted that certain obscure diseases, such as scurvy and beriberi, are frequent among those who are compelled by force of circumstances to subsist for long periods on an unvaried diet. This is true even though their food evidently contains sufficient quantities of the three most prominent dietary ingredients – the carbohydrates, fats, and proteins. Moreover, the victims of these peculiar ailments are often cured by a trifling quantity of some new foodstuff. Whole crews of vessels making prolonged voyages have sometimes been stricken down with scurvy, then miraculously cured by a few raw potatoes, or a little lemon juice.

Since very minute quantities of such materials are sufficient to produce a cure, it is evident that they do not act by supplying the needs of the body for the more obvious dietary essentials. The vitamines are apparently organic substances which are assimilated in very small amounts, or which act by their mere presence to enable the other dietary ingredients to be assimilated – as though they were nutritive catalyzers.

Whatever the chemical nature of the vitamines may be, numerous researches with experimental animals show that vitamines differ among themselves in their solubility in different solvents, their resistance to destruction by heat or alkali, and in other ways. The three kinds first distinguished (A, B, C) are all necessary to normal growth and reproduction. In addition, vitamine B, which occurs especially in green vegetables, plays an important part in promoting appetite. Scurvy develops in the absence of vitamine C, and is cured by the use of foods containing it. It is less resistant to heat than the other vitamines – a reason why pasteurized milk is not desirable for small children, unless supplemented by orange juice, or other material rich in vitamine C.

It has recently been found that alfalfa and the roots of sprouted barley contain a substance (or a mixture of substances) a mere trace of which is capable of stimulating the growth of the yeast plant in a very remarkable way. This "growth catalyzer for yeast" has been named **bios.** Growth catalyzers for bacteria and for rats (vitamin D) appear also to exist. In addition, there is some evidence for the existence of still another vitamin, necessary for reproduction though not for normal growth. This appears to be present in a number of common cereals.

The body appears to be unable to synthesize the vitamins, but must find them, ready-made, in the food. On the other hand, there appears to be no reason why one should eat patent cereal preparations or yeast cakes through fear of failure to obtain vitamines. A diet sufficiently varied, with a proper supply of fruits, vegetables, dairy products, and whole cereals should supply these unidentified dietary essentials quite automatically.

393. Standard Diets.—There seems to be little ground for the common assumption that appetite may serve as a safe guide to the quantity and kind of food that one's diet should include. Appetite, if it does anything, may perhaps indicate the body's requirement for energy; but that this requirement may easily be exceeded is shown by the fact that many persons of sedentary occupation grow corpulent. The excess of fuel, instead of being burned up day by day, goes to overburden the tissues with a useless store of fat. In no case is appetite any measure of the body's needs for protein, phosphorus, calcium, iron or the several vitamines.

The energy and protein requirements of an adult person may be calculated with sufficient accuracy from the data of the preceding pages about 2500 to 3000 large calories, and 75 g. of protein per day, for a man of average weight, at light or moderate physical exercise. Heavy exercise may more than double the energy requirement, but the protein requirement will remain unchanged, unless the exercise actually builds new muscle. **There is nothing to indicate that muscular tissue wears out any more rapidly when used than when at rest, provided that it be supplied with a sufficient amount of non-nitrogenous material (fat and carbohydrate) to furnish the energy expended in exercise.** But, since the effect of exercise is usually to cause one to take more food of much the same chemical composition as before, increased exercise in practice means an increased intake of protein foodstuffs.

One of the important problems in compounding a ration is the maintenance of a proper ratio between protein and the other constituents of the diet. This is most conveniently calculated with the help of the **nutritive ratio—the ratio of calories derivable from the whole diet to those derivable from protein alone.** Since fat has $2\frac{1}{4}$ times the fuel value of either carbohydrate or protein, the nutritive ratio of a food is plainly $(C+P+2\frac{1}{4}F)\ P$; in which C, P, and F represent the percentages of the three principal constituents of the food. When the nutritive ratio of the principal foods is known, the calculation is easy. Foods with a high nutritive ratio are combined with those with a low nutritive ratio, to give a diet with a proper average value.

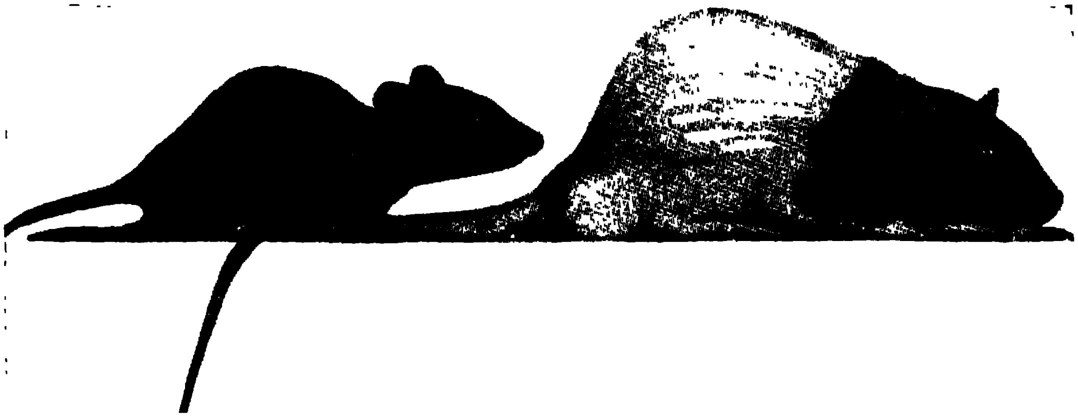


FIG. 96—Research in biochemistry University of Wisconsin. Two rats of the same sex and litter. The rat on the left received a diet deficient in one of the essential amino acids The one on the right obtained a little of this substance, in addition to its other food.

There is fortunately little cause for fear that when protein is present in the diet in sufficient quantity it may still be deficient in quality. **Certain individual proteins, in purified form, are known to be incapable of sustaining life or maintaining growth unless combined with other proteins.** It appears that they lack certain essential amino acids (trytophane, cystine, lysine) which the body seems to be unable to synthesize, but must find ready made in the fragments of the protein molecules that are digested. In any normal diet, however, and even in individual grains, it is probable that the different essential amino acids are all present in the mixture of proteins that is present.

Children require relatively larger amounts of both energy and protein than are needed by adults. A child of ten, for example, may require two-thirds the adult ration of each of these essentials. They also need a more than proportionate amount of the inorganic elements most likely to be deficient namely phosphorus, calcium, and iron. Of special importance, too, in the feeding of children, are the **vitamines.**

The preceding brief discussion is sufficient to show that the calculation of a proper standard diet is a very complicated matter. Most of us are overfed in protein, and perhaps in energy, while running some risk of obtaining an insufficient supply of phosphorus, calcium, and iron. A little more thought to such matters, with the guidance to be had from one of the text-books on the subject, would perhaps improve the health of the average man, and would certainly save him money. In raising farm-animals for the market, such considerations, of course, make all the difference between profit and loss.

EXERCISES

1. Compare the successive steps in the digestion of starch with the chemical process by which glucose sirup (§ 369) is prepared.

2. Zein, the chief protein of corn, contains about 0.6 per cent sulfur. Assuming it contain but one atom of sulfur in a molecule, calculate its molecular weight.

3. By what is known as the Kjeldahl method, the nitrogen contained in 5 g of a foodstuff is converted into ammonia. This proves just sufficient to neutralize 20 cc. of N/10 acid. Calculate the percentage of nitrogen and "crude proteid" in the foodstuff.

4. Tabulate the digestive enzymes mentioned in this chapter according to the nature of the materials that they alter and the products that they form.

5. From the data of Appendix B calculate the nutritive ratios of four different foods of dissimilar character.

6. From the available energy value of protein (about 4 large calories per gram) calculate the nutritive ratio of a food which willl supply 3000 large calories and 75 g. of protein a day.

7. Two foods have nutritive ratios of 4 and 12. What weight of each will need to be present in 100 parts by weight of a mixture of nutritive ratio 10?

8. Which require a ration with the higher nutritive ratio, and why: young animals, growing rapidly; or mature animals, being fattened?

9. Explain what is meant by "respiratory coefficient," and tell something of its significance.

CHAPTER XXX

SILICON AND BORON

394. Carbon and Silicon Compared and Contrasted.—Now that we have completed our survey of carbon, let us turn to silicon, the element revealed by the periodic table as carbon's next of kin. The *resemblances* between the two elements are striking and important:

1. Both are non-metallic elements, melting at a very high temperature (Si, 1420°; C, over 3600°).

2. Both, in conformity with their non-metallic nature, form inactive acids, with similar series of salts, the carbonates and metasilicates.

3. Both have, almost uniformly, a valence of four, and consequently form numerous compounds of corresponding formulas:

CH_4	methane	SiH_4	silico-methane
C_2H_6,	ethane	Si_2H_6	silico-ethane
CCl_4,	carbon tetrachloride	$SiCl_4$,	silicon tetrachloride
$CHCl_3$,	chloroform	$SiHCl_3$,	silico-chloroform
CO_2,	carbon dioxide	SiO_2,	silicon dioxide

But *contrasts* between the two elements are quite as impressive as resemblances.

1. Silicon is more than one hundred times as abundant as carbon; and its compounds, the rock-forming minerals, make up most of the solid crust of the earth.

2. Yet what carbon lacks in abundance it makes up in capacity for entering into combination. Over two hundred thousand different carbon compounds are known and catalogued; and hosts of others exist in nature, which have not yet been isolated and analyzed. The natural silicates, on the other hand, with such silicon compounds as have been prepared artificially, fall short of a thousand. This failure of silicon to duplicate the astonishing

versatility of carbon suggests that silicon atoms unite much less readily with each other to form extended chains and stable rings than do carbon atoms.

395. The Plutonic Rocks.—We must make a brief excursion into the realm of geology, if we are to get any clear understanding of the nature of the minerals that serve as raw materials for the great silicate industries—the manufacture of glass, bricks, pottery, porcelain, and cement.

In the interior of the earth, at a depth of say eighty or a hundred miles, there probably exists a region of intensely hot rock, confined under a tremendous pressure, due to the weight of overlying material. We do not know whether this rock is actually molten, for we have no way of determining the temperatures that exist at such great depths; neither can we estimate the effect of pressure in raising the melting points, nor that of dissolved gases in lowering the melting points of minerals. We are moreover at a loss to determine whether this **rock magma** is everywhere sensibly the same, or whether it varies in composition from place to place or from depth to depth.

Whatever the answers to such questions may be, we are certain that the magma is the source of all the rocks, minerals, and soils that cover the surface of the earth. Perhaps it is also the source of the ocean and the gases of the atmosphere. In many places it has risen under pressure through cracks or fissures in the overlying layers—approaching near enough to the surface to be laid bare by subsequent erosion; or bursting forth in a fluid torrent from the crater of a volcano. Thus are formed the **plutonic** (or igneous) **rocks,** named after Pluto, the god of fire and of the underworld. They differ in chemical composition from place to place, due to variations in the original magma; or to changes induced by contact with the rock-walls between which they have risen; or to a sorting or segregation brought about by deposition of crystals or escape of gases, while the material still was fluid. Even at the same place, successive outflows or extrusions often vary greatly in chemical composition.

396. Different Physical Forms of Rock Material.—The physical characteristics of the plutonic rocks of a single chemical type may also differ widely. **All magma at great depths appears to hold vast quantities of gases and water vapor, retained in solution under**

enormous pressure. When this material has worked its way upward toward the earth's surface, a fissure may open suddenly and relieve the pressure, releasing vast quantities of superheated gas and water-vapor with an earth-shaking explosion, and blowing the whole contents of the volcanic throat skyward into atomized spray. The sudden cooling of this finely divided material produces volcanic ash, which may rain down from the heavens for many days from the time of the original explosion, or be carried by winds entirely around the earth. Any magma which fails to be completely atomized may still be thrown into violent effervescence by the escape of gases; and if suddenly congealed while in this condition, the result is **pumice**—which has the appearance of petrified foam. Finally, when the foaming is past, there may be a quiet outflow of lava, cooling quickly to a uniform glassy mass, or setting slowly to a mass of interlocking crystals. Ash, pumice, glass, or crystal-matrix—all may be but different physical forms of identical chemical material.

397. Minerals.—The magmatic outflows and extrusions from which the plutonic rocks arise, are commonly regarded as **solutions of the oxides of the more plentiful metals** (Al, Fe, Ca, etc.) **in *silica*** (SiO_2). But what the real state of combination may be between the constituents of the molten magma—whether the calcium, for example, is present as a silicate or an aluminate, or both—we find it quite impossible to state. The most we can do is take note of the compounds that form and separate as the solution cools.

On the average, the earth's crust contains about two equivalents of metallic oxide for each molecule of silica. In other words, **the solid rocks have an average composition approximating salts of metasilicic acid,** H_2SiO_3 (§ 398). But many individual rocks depart rather widely from this average. Rocks, for the most part, are not definite chemical compounds—though if they have cooled slowly enough they may contain crystals which are definite compounds, embedded in a glassy ground mass (supercooled liquid). Thus granite consists of three different types of crystals.

The chemical individuals that go to make up the igneous rocks, or that are derived from the original magma by a process of crystallization are called **primary minerals.** But in addition to these, we know a great many **derived or secondary minerals,** produced by alteration of the primary minerals, through heat, pressure, or circulating water. Thus **feldspar,** the principal constituent of granite, may be altered to mica and quartz by heat and pressure; or may produce clay by weathering.

398. Classification of the Silicate Minerals.—It is often convenient to consider the silicate minerals as being formed by combination of the different metallic oxides (CaO, FeO, Fe_2O_3, Al_2O_3, K_2O, etc.) with silica (SiO_2). Among those relatively rich in metallic oxide are the **orthosilicates,** salts of the hypothetical orthosilicic acid (H_4SiO_4).* Examples are Mg_2SiO_4 and Zn_2SiO_4. With just half this relative amount of base-forming oxide are the **metasilicates,** salts of the hypothetical metasilicic acid (H_2SiO_3). Examples are Na_2SiO_3, $CaSiO_3$, $Al_2(SiO_3)_3$, etc.

Minerals relatively rich in silica are called **polysilicates.** Among these the **trisilicates,** salts of the hypothetical trisilicic acid ($H_4Si_3O_8$) are important.

Many, but not all, of the **feldspars** are trisilicates. They form the most abundant group of minerals in nature and make up about 60 per cent of the igneous rocks of the earth's crust. Potash feldspar, or **orthoclase,** for example, with the formula $KAlSi_3O_8$, forms the large, oblong, pinkish crystals conspicuous in ordinary granite.

399. Quartz and Other Forms of Silica.—Silica, or silicon dioxide, SiO_2, is known in at least six different crystalline forms. Of these the most common is **quartz,** which is found in large transparent crystals, which are hard enough to scratch glass. Quartz is a mineral second only to the feldspars in abundance, and is estimated to compose about 12 per cent of all the igneous rocks of the earth. It is also formed as a secondary mineral by deposition from solution. Quartz and the amorphous or hydrated forms of silica are very often colored by traces of organic matter (smoky quartz) or by oxides of manganese or iron (amethyst, agate, jasper, onyx).

Certain minute aquatic organisms (diatoms, infusoria) and certain varieties of sponges, develop silicious skeletons which accumulate on the ocean bottom when the organisms die. Deposits up to a thousand feet in thickness have been found in various parts of the United States. This material is called *infusorial or diatomaceous earth* (*kieselguhr*). Mixed with a little soap and sodium carbonate it is used as a scouring powder (metal polishes); and like fuller's earth, an extremely fine clay, it finds application for adsorbing and removing the coloring matter from edible oils.

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* The different classes of silicates illustrate the fact that well-defined salts of a particular formula often exist, while the acid from which they appear to be derived is unknown (§ 103).

Flint is composed of sponge spicules or other silicious organic residues cemented together by colloidal silicic acid and hardened by slow dehydration under pressure.

400. Fused Silica.—Quartz is converted into other crystalline forms of silica at high temperatures; but it proves impossible to melt any of these below 1670° C., a temperature far above anything attainable with a gas- or coke-fired furnace. But chemical apparatus of **fused silica,** manufactured by fusing sand in an electric furnace, is now of importance in the laboratory as a substitute for platinum. In the chemical industries, sulfuric acid is now concentrated by being passed over a series of heated shelves or basins built of fused silica, and arranged in the form of a cascade. Transparent fused silica has the advantage over glass of transmitting both visible and ultraviolet light.

Fused silica is cheaper than platinum, and less likely to lose weight on being heated strongly (§ 604). It has a smaller coefficient of expansion, a property that makes it less likely to crack on sudden cooling. A fused silica crucible may be heated red hot and plunged into cold water without being injured. The chief disadvantage of such material is its gradual transformation, at temperatures above 1100° C., into crystalline varieties of silica, of inferior mechanical strength.

401. Hydrated Silica.—When finely powdered silica is heated for a long time with water, best in an autoclave (§ 86), at temperatures above 100° C., a small part of it dissolves, forming a colloidal solution (*sol*); while the remainder absorbs 15 to 20 per cent of water, forming a transparent gelatinous mass or *gel* (§ 382). Again, when a soluble silicate (water-glass, § 105) is decomposed with an acid, there is obtained a highly hydrated gelatinous form of silica,* which may be made to lose water gradually and continuously by squeezing it in a press, or even by exposing it to a dry atmosphere. Eventually but a few per cent of water may remain. Thus we know all possible stages between completely anhydrous silica and highly hydrated silica gels, containing as much as 98 per cent of water. Nowhere is there evidence of the formation of a hydrate of silica, of invariable composition or definite formula (compare the case for $Al(OH)_3$, § 471).

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* If the solution is very dilute there may not be any precipitate formed at first. The silicic acid is then in colloidal solution. On long standing, or by adding an electrolyte, the sol eventually becomes changed to gel.

402. Asbestos, Talc, and Mica.—Any silicate mineral having a fibrous structure is classified as *asbestos*, regardless of its chemical composition. The two most important varieties are **hydrated magnesium silicates.** One of these is short fibered, but very infusible and acid-resistant. It is accordingly used for packing steam-pipes and furnaces, and in the chemical industries for filtering acids. The longer fibered, less heat-resistant variety, coming principally from Eastern Canada, is woven into fireproof fabrics.

Closely related to asbestos is **talc,** also a hydrated magnesium silicate. This is a white mineral, with a flaky texture. It is soft enough to be scratched with the finger nail, and so smooth as to be almost greasy to the touch. It is used in cosmetics, for filling paper (§ 371), for finishing leather, and for polishing glass and metals. **Soapstone,** used in electrical switchboards, and for sinks and table tops, is a relative of talc. The United States produces over 100,000 tons of the two minerals each year.

Mica is a familiar transparent mineral used in thin plates on stove doors. This is **muscovite,** or potash mica, a hydrated potassium-aluminum silicate. Its crystalline condition permits it to be split into sheets as little as 1–2500th of an inch in thickness (which is thinner than most tissue paper).

The electrical industries use an amber-colored variety of mica known as phlogopite, from Eastern Canada. In this a part of the aluminum of the transparent variety is replaced by magnesium and ferrous iron. It has nearly the same hardness as metallic copper, and is therefore useful as an insulator between the commutator bars of dynamo electric machinery. Wireless telegraphy calls for large quantities in the manufacture of condensers.

403. Zeolites.—The zeolites are a group of hydrated sodium-aluminum-calcium silicates, of indefinite composition, occurring in many weathered rocks and soils. They are remarkable in having a large part of their sodium but loosely held—apparently by adsorption (§ 327)—and therefore readily replaced by other elements. Thus a solution of a potassium salt, percolating through a bed of zeolitic material, will yield up its potassium to the latter, in exchange for sodium:

$$\text{Na}\cdot\text{Zeolite}+\text{KCl}\rightarrow\text{K}\cdot\text{Zeolite}+\text{NaCl}.$$

The fact that potassium is retained by most soils, while sodium tends to be leached away, may be partly due to sodium zeolites in the soil, which offer up a portion of their sodium, in exchange for potassium. Artificially prepared zeolites may be used for softening water (§ 462).

404. Melting Points of the Silicates.—The industrial applications of an artificial silicate are often determined by its melting point. The oxides that enter into its composition are themselves, for the most part, extremely infusible:

	MgO	CaO	Al_2O_3	SiO_2
Melting Point, °C.	2800	2570	2050	1670

But when any one of these has received an addition of a small amount of one or more of the others, its melting point is lowered. This is an illustration of the general principle that **the melting point of a pure substance is always lowered by the addition of a small amount of something of different chemical nature from itself.**

But if more than a few per cent of the other oxides is added to any one of the pure substances listed above, its melting point may begin to *increase*, on account of the formation of difficultly fusible compounds. With some of the simplest silicates the variations in fusibility with varying composition have been fully worked out, and we are able to predict the melting point of any given sample from its chemical analysis. Speaking in general terms, the polysilicates (§ 402) melt more readily than the basic silicates—largely because silica itself melts at a lower temperature than the other oxides concerned. It happens, for example, that the most fusible calcium-aluminum silicate is a mixture containing 67 per cent SiO_2, 13 per cent Al_2O_3, and 20 per cent CaO (not a definite compound, but roughly $3CaO\cdot Al_2O_3\cdot 9SiO_2$).

The fact that silicates with a high percentage of silica have comparatively low melting points is found useful in the preparation and purification of metals, impurities being removed in the form of readily fusible, highly silicious slags. In glass-making, too, a considerable excess of silica is necessary to secure a mixture which will become fluid enough at the temperature of the melting furnace to permit air bubbles and undissolved particles to rise to the top and be skimmed away A glassy appearance is very characteristic of all the highly silicious artificial silicates; the more highly basic materials, such as furnace cinders, and Portland cement, are quite dull and opaque Nevertheless at the temperature of an electric arc even these melt down smoothly to slags, that have a glassy appearance on solidifying

405. Water-Glass.—The simplest of the artificial silicates are those prepared by fusing sodium or potassium carbonates with sand:

$$Na_2CO_3 + 4SiO_2 \rightarrow Na_2O \cdot 4SiO_2 + CO_2 \uparrow .$$

The result is a glassy solid solution (§ 92) having an average composition corresponding approximately to the above formula. If this material is digested with water in an autoclave (§ 86) at temperature above 100° C., it dissolves very readily. On cooling to room temperature we have a thick, viscous solution, moderately alkaline toward indicators, and technically known as *water-glass*.

Water-glass solution is used (1) as a cement, (2) for waterproofing stone surfaces: (3) as an adhesive in making pasteboard boxes; (4) as a filler in the manufacture of laundry soap (§ 363), and (5) for preserving eggs. Vats to contain dilute acids are frequently lined with tile set in a paste of powdered talc and water-glass.

406. Lime-Soda Glass.—Any mineral substance which breaks with a characteristic glassy fracture, and possesses a vitreous or glassy luster, with some degree of transparency, is often referred to in a loose sort of way as a *glass*. Ordinary soft, or lime-soda glass, used for window panes and bottles, is a sodium-calcium silicate. But useful glasses have been prepared containing none of the three elements Na, Ca, Si.

The most important raw materials for the manufacture of common glass are *calcium carbonate*, *sodium carbonate*, and *quartz*. These must be very finely powdered and intimately mixed. If the glass is to be colorless the raw material should be free from more than traces of iron. When such a mixture is heated in a furnace the silica decomposes the carbonates, expelling carbon dioxide, and after a few hours the contents of the crucible melt down into a clear liquid, which is purified by skimming and then cast or blown into molds.

Sodium sulfate, in the presence of powdered coke, which serves as a reducing agent, is often substituted for sodium carbonate in the manufacture of glass.

$$a\mathrm{Na_2CO_3} + b\mathrm{CaCO_3} + c\mathrm{SiO_2} = a\mathrm{Na_2O} \cdot b\mathrm{CaO} \cdot c\mathrm{SiO_2} + (a+b)\mathrm{CO_2}.$$

The best lime-soda glasses contain from about 1½ to 2 molecules of SiO_2 for every equivalent of base. Of the total base present, from about 0.4 to 0.6 is Na_2O, and the remainder CaO. They therefore approximate the formula $Na_2O \cdot CaO \cdot 6$ to $8SiO_2$. But the Na_2O and CaO may be replaced in part or entirely by some other combination of bases, including K_2O, ZnO, BaO, or PbO; and the SiO_2 by other acid anhydrides, chiefly B_2O_3 and P_2O_5. The glasses thus obtained have various special properties.

Colored glass is made by the addition of oxides of the heavy metals, to form colored silicates. Cobalt oxide gives a blue color; selenium dioxide or gold oxide, a ruby-red; cupric oxide, a blue under oxidizing conditions, or a dull red (due to metallic copper) under reducing conditions; chromium trioxide, a green; silver oxide, a yellow; manganese dioxide, a violet.

407. Optical Glass.—Glass of a sort was known even to the ancients. The earliest glasses appear to have been of very inferior quality: dark and non-transparent; full of undissolved particles; and subject to destruction by crystallization (*devitrification*). Glass which is to be used for lenses must be almost colorless, and uncommonly free from defects due to enclosed air bubbles, solid particles, or lack of uniform composition. These requirements mean that optical glass must be stirred for a long time in the melting-pot, and cooled very slowly during a period of five or six days. But glass satisfying the exacting requirements of modern optical instruments is only half a century old, the first of the recent advances being due to Schott and Abbe, at Jena, who determined the effect of replacing lime and soda by other bases.

Unfortunately these and later investigators in Germany and Austria concealed the more valuable part of their discoveries, and at the outbreak of the World War the Allies were unable to produce the optical glass that they needed for periscopes, range-finders, searchlight mirrors, gun-sights, and photographic lenses for aerial reconnaissance. In this emergency, American chemists were able in a few months to duplicate the most important achievements won by Central Europe during two generations. Optical glass recently produced in the United States is superior to any that has ever been imported.

The older optical glasses were classed as *crown* (lime-soda-potash) and flint (lead oxide-soda-potash) glass. By a combination of these two kinds of glasses it is possible to produce a lens that will form an image that is both *anastigmatic* (free from distortion) and *achromatic* (free from rings of color). In the modern optical glasses a part or all of the silica is often replaced by boric oxide (B_2O_3) or phosphoric oxide (P_2O_5); and a part or all of the lime and soda by the oxides of barium, zinc, magnesium, or even aluminum.

408. Chemical Glassware.—Chemical laboratory apparatus needs to be (1) mechanically strong; (2) less liable to break than ordinary glass when subjected to sudden temperature changes;

and (3) as nearly insoluble as possible in water, dilute acids, or dilute alkalies. Increased resistance to mechanical and thermal shocks is obtained by substituting B_2O_3 for a part of the SiO_2 of common soft glass, and decreased solubility by partly replacing the alkalies (Na_2O and K_2O) by ZnO and Al_2O_3, or even by Sb_2O_3.

Pyrex glass, a boro-silicate glass of American manufacture, is superior in the three qualities we have mentioned to the best of the Jena laboratory glass, which was in almost exclusive use in our laboratories prior to 1914. It is especially valuable in accurate quantitative analysis, since it is almost free from calcium and other alkaline earth metals, which ordinary glass yields up to boiling aqueous solutions in very appreciable quantities. It is more infusible than ordinary glass, but may be worked readily in an oxy-acetylene flame. *Combustion-tubing*, which should have a still higher melting point, has a part of the Na_2O of soft glass replaced by K_2O and BaO; and a part of the SiO_2 by B_2O_3.

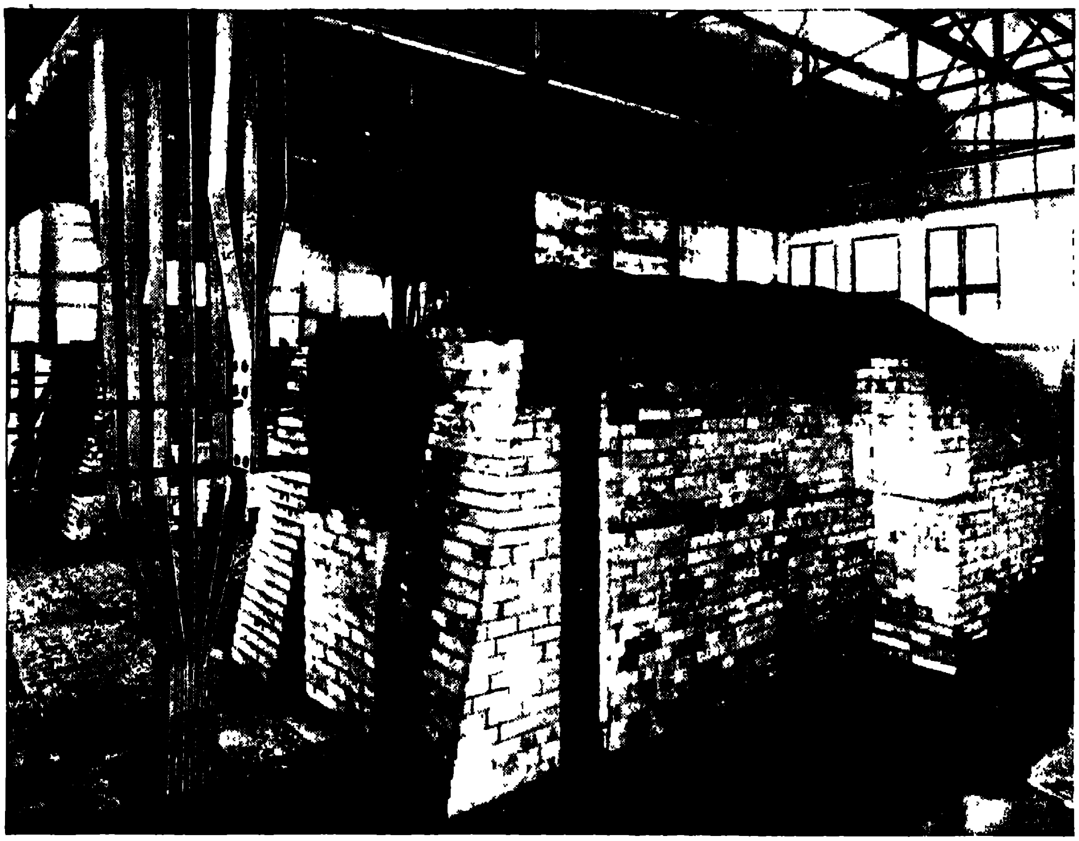

FIG. 97.—A carborundum furnace Note the heavy copper conductors in foreground. Each furnace consumes several hundred horse-power.

409. Carborundum.—Silicon carbide, or **carborundum, SiC,** is prepared by heating silica with an *excess* of coke to about 1800° C.

$$SiO_2+3C=SiC+2CO.$$

An electric furnace is employed (Fig. 97) with water-cooled ends and fire-brick walls, containing a charge of mixed quartz sand, coke and sawdust, together with a little common salt, which has the effect of removing iron and other impurities in the form of volatile chlorides. A conducting core of graphitized coke, buried in this mixture, becomes incandescent by the passage of the current, and after a few hours is found to be surrounded by carborundum crystals, SiC.

Carborundum is produced in crystalline masses, of a violet-black, iridescent hue, rather brittle, but almost as hard as diamond. The powdered material, with a little clay or feldspar as a binder, is molded into grinding wheels, which after firing at a high temperature may be used for grinding automobile cylinders and other metal parts to exact dimensions.

410. Elementary Silicon.— Elementary silicon is prepared on a large scale by heating sand with coke in an electric furnace consisting of a fire-brick box lined with carbon (Fig. 98). A set of heavy graphite electrodes, lowered from the ceiling, form an arc in the interior of the charge. At the high temperature thus reached the silica is quickly reduced to elementary silicon, which collects at the bottom of the furnace in molten form, and is tapped out from time to time.

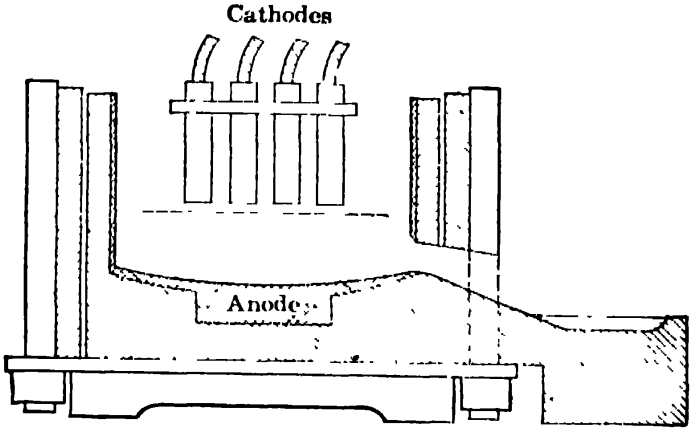

Fig. 98.—A silicon furnace.

Silicon is a brittle solid of a silver-grey luster and high melting point (1400° C.), a little heavier than sulfur, but only about a third as heavy as copper and iron. It is extremely resistant to acids, but is readily dissolved by alkali hydroxides to form soluble silicates. It has been used to a slight extent (1) in acid-proof castings; (2) as a substitute for carbon in the reduction of iron, chromium, and other metals from their ores, when it is desired to produce carbon-free alloys; (3) for mingling with common steel to produce silicon-steel (§ 501).

Of greater commercial importance than silicon itself is *ferro-silicon*, an alloy containing 10 per cent to 75 per cent iron. It is produced in an electric arc furnace in the same way as pure silicon; or else (for low percentages of silicon) by reduction in a blast furnace (§ 492). Its most important use is in steel making, to remove the oxygen which is dissolved in molten steel, and which would cause imperfections in steel ingots or rails, if allowed to remain (§ 496). We have already noted the use of ferrosilicon in generating hydrogen for military purposes (§ 70). Iron-silicon alloys with 10 or 15 per cent of silicon are used for acid-resisting pipes, kettles, and other castings (*tantiron*, *duriron*). These are very hard and almost acid-proof, but are brittle, and liable to crack if incautiously heated.

BORON

411. Boron, and Boron Minerals.—A very interesting element is *boron*. From its position at the head of column IIIA, in the periodic table, we should expect it to be related to aluminum. It does, in fact, have the same valence as aluminum (three); but in most of its chemical properties is non-metallic and very closely related to silicon. Moreover, its oxide replaces silicon dioxide in many glasses, glazes, and enamels—a practical reason for its consideration here.

Elementary boron has been prepared by reduction of the oxide, B_2O_3, in a covered crucible, with metallic sodium, potassium, magnesium, or aluminum (§ 478).

Boron occurs in traces in a great many igneous rocks. The workable deposits of boron minerals occur mainly in dry countries, the most important ones in the United States being *borax*, or sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$; and *colemanite*, or calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$. These occur in almost inexhaustible quantities in the alkaline lakes and deserts of Nevada and Southern California.

412. Borax.—***Borax***, or **sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$,** is the most important salt of boron. It reacts alkaline toward indicators, since the several boric acids, to be mentioned in the next section, are all very inactive, and their salts are all partially hydrolyzed by water. This alkaline reaction makes borax useful as an ingredient of washing powders and patent cleansers. It moreover softens water (§ 461), precipitating insoluble calcium and magnesium borates. Other uses are as a flux in soldering, and in the preparation of enamels and resistant glasses (§ 408).

413. Boric Acids.—When a concentrated, warm solution of borax is decomposed with a dilute acid, double decomposition takes place, forming **boric acid** (orthoboric acid),* H_3BO_3. This is a slightly soluble substance, which crystallizes out in glistening white flakes as the solution cools. It is somewhat volatile with steam, a fact that accounts for its presence in jets of water vapor that issue from the ground in the neighborhood of certain volcanoes. It is used in medicine, in antiseptic washes.

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* Also called *boracic* acid, particularly in medicine.

If orthoboric acid is heated in the air, it loses water, forming metaboric acid, HBO_2, then tetraboric acid, $H_2B_4O_7$, and finally boric acid anhydride, or boron trioxide, B_2O_3. These all revert to orthoboric acid when dissolved in water. The important borates are salts of metaboric and tetraboric acid.

EXERCISES

1. Summarize the chief points of resemblance and contrast between carbon and silicon.
2. Present some arguments for or against the existence of a definite compound of the formula H_2SiO_3.
3. What percentage of potassium oxide is contained in pure potash feldspar?
4. What is meant by a hypothetical acid? Give two examples of such acids containing other non-metallic elements than silicon.
5. Write an equation for the preparation of water-glass by digesting powdered silica with caustic soda in an autoclave.
6. A lime-soda glass is to have the composition $Na_2O \cdot CaO \cdot 6SiO_2$. What weight each of anhydrous sodium sulfate, limestone, and quartz will need to be taken for each ton of glass, assuming 10 per cent of the soda to be lost by volatilization and skimming?
7. With anhydrous sodium carbonate at 5 cents a pound, what must be the price of anhydrous sodium sulfate to compete in glass manufacture, assuming the two salts to be of equal desirability, aside from their different content of Na_2O?
8. What are some of the principal optical characteristics desired in glass for lenses? What are the constituents of optical glass.
9. List three important commercial abrasives in the order of decreasing hardness, giving the chemical formula and principal uses of each.
10. Give equations to show the use of ferro-silicon in preparing hydrogen, with regeneration of the sodium hydroxide.
11. Write and balance an equation for the preparation of boric acid from borax.
12. Anhydrous borax is fused with its own weight of powdered quartz and half its own weight of chalk. Calculate the percentage composition of the product in terms of its chief constituent oxides (Na_2O, CaO, SiO_2, B_2O_3).
13. Write equations for the preparation of ferro-silicon from quartz and hematite. Why may not these two equations be combined into one, by addition?
14. Describe in detail laboratory methods by which it would be possible to produce alumina, potassium chloride, potash alum, and silica from potash feldspar, after first fusing the material with sodium carbonate. Write all equations.
15. In what proportions must anhydrous sodium carbonate and powdered quartz be taken to produce water-glass of the composition $Na_2O \cdot 4SiO_2$?

What weight of raw material will be needed for a liter of water-glass solution of specific gravity 1.7, containing 50 per cent solid matter?

16. A silicate mineral is finely powdered and evaporated to dryness with a mixture of HF and conc. H_2SO_4. Write equations to show what becomes of the silica and lime, originally present in the mineral

17. What raw materials would you suggest for preparing a blue enamel (a fusible glass) for jewelry?

Part III

THE METALS

CHAPTER XXXI

GENERAL CHEMISTRY OF THE METALS *

In the preceding chapters we have outlined the chemistry of the non-metals. These occupy the upper, right-hand corner of the periodic table, and include fourteen elements in all. We have also made brief mention of the six inert gases, occupying the extreme left-hand column of the table (§ 181). There remain for consideration the **metals**—about 65 in all, or more than two-thirds the total number of elements known. The present chapter will give a general survey of the chemical and electrochemical characteristics of the metals, the principles involved in preparing them from their ores, and in preparing their salts. Then, in following chapters, we shall consider the alkali and alkaline earth metals, and a few heavy metals of outstanding importance. The properties of all the rest may be inferred in considerable detail from their positions in the periodic table.

414. The Metals and the Periodic Table.—Review §§ 167, 168, 260. Physically, metals are distinguished from non-metals by their **" metallic " luster,** their **conductivity for heat and electricity,** and their capacity for being rolled or hammered into thin sheets (**malleability**) or drawn into wire (**ductility**). The different metals, however, possess these properties to very different degrees. When very finely divided, they nearly all lose their luster and become black. Silver is sixty times as good a conductor of electricity as mercury; and tin, when somewhat heated, becomes almost as brittle as sulfur. Certain non-metals, furthermore, are not entirely devoid of the physical characteristics of metals. Arsenic and selenium, for example, though non-metallic in their chemical behavior, have a bright luster, and are reasonably good conductors of electricity.

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* Some of the topics of this chapter are best omitted with elementary classes; and others, perhaps, are best postponed to be considered in connection with the metallurgy or electrochemistry of particular elements.

On the whole, therefore, metals are most readily recognized as such by their chemical properties:

1. Metals form oxides that combine directly with non-metallic oxides, or dissolve in acids, to form salts—sulfates, nitrates, acetates, etc. Such metallic oxides as are soluble in water dissolve to form alkaline solutions.

Write equations for the formation, in the two ways suggested here, of potassium sulfate from potassium oxide, and of calcium nitrate from calcium oxide.

2. Metals combine directly with the halogens to form halides, which are either not hydrolyzed at all, when dissolved in water (halides of the light metals),* **or are but incompletely hydrolyzed** (halides of the heavy metals). Halides of the non-metals, on the other hand, are commonly completely hydrolyzed (§ 191).

Indicate which of the following halides are not hydrolyzed at all, which only partially, and which completely: calcium iodide, ferrous chloride, potassium fluoride, phosphorus tribromide, silicon tetrafluoride, aluminum bromide.

What is the reaction toward indicators (§ 111) of the solution formed in each of the above cases, and why?

Formulate one of the cases in which hydrolysis is incomplete, as a reversible reaction, first in terms of molecules (§ 113), then in terms of ions (§ 269)

3. Metallic ions commonly migrate toward the cathode (§ 167), **when an electric current is passed through a solution of a base or salt.** Nevertheless, many heavy metals, especially in their higher valences, enter into groups that migrate toward the anode. Thus, when a current is passed through a solution of potassium chromate, K_2CrO_4, the potassium moves toward the cathode, and the chromate radical toward the anode.

4. Metals commonly displace other, less active metals, from solutions of their salts, but never displace the most pronounced non-metals:

$$CuSO_4+Fe=FeSO_4+Cu\downarrow .$$

Write this equation in ionic form. Explain it as a transfer of electrons.

These properties of the metals are all implied by the statement that **atoms of the metals tend to lose electrons and thus form posi-**

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* The *fluorides* of the light metals are somewhat hydrolyzed, however, for hydrofluoric acid is very inactive.

tively charged ions; while atoms of the non-metals (or groups of non-metallic atoms) tend to gain electrons, and thus form negatively charged ions.

The light metals are definitely metallic by all the tests we have mentioned. The heavy metals, however, merge into non-metals by imperceptible degrees. Thus, the heavy line that commonly appears in the periodic table to separate these two classes of elements cannot be drawn very accurately. Arrows in the periodic table indicate the **order of increasing metallic properties,** or **order of increasing electropositive character.** Strictly understood, this is the order of increasing activity (as metals) or increasing tendency of metallic atoms to part with electrons and assume the condition of positively charged ions. It is the order of the electrochemical series (§§ 72, 422), read from below upward.

Nevertheless, the expression "order of increasing metallic properties" is often used in a loose way to indicate the order of increasing degree of ionization or activity (as bases) of the hydroxides of metals; or the order of increasing difficulty in hydrolyzing salts, or in decomposing salts by heat (to form basic salts or oxides); or even the order of increasing scarcity of compounds in which the given element forms part of a non-metallic radical (anion). The order of increasing metallic properties by these different tests is only roughly the same.

All the salts of the heavy metals are more readily hydrolyzed than those of the light metals. The fact that all aluminum salts are partially, or even almost completely hydrolyzed is proof that aluminum, though physically light, is chemically to be classed among the heavy metals.

In the outlying portions of the periodic table, among the light metals and non-metals, the chief resemblances are between elements in the same **vertical column.** Among the heavy metals, however, resemblances are also to be found between elements in the same **horizontal row.** Thus, chromium (Cr) is not only related to molybdenum (Mo) and tungsten (W), elements occupying positions immediately below it, in column VI*B*; but also to vanadium (Vd), on its left; and to manganese (Mn), on its right.

In the transition group (VIII) these "horizontal relationships" are the important ones, while the "vertical relationships" are almost absent. Thus, iron, cobalt, and nickel are closely related to each other, but have little in common with ruthenium, rhodium, and palladium, or with osmium, iridium, and platinum.

The heavy metals are all to some degree related to the elements of the outlying groups of light metals and non-metals, as indicated by sloping lines in the table. Group IV*A* is very closely related to Group IV*B*; but the degree of relationship between "main group" and "sub-group" decreases with group numerals above and below four. Thus, Group I*A* has little in common with group I*B*; and Group VII*A*, little in common with Group VII*B*.

It is interesting to notice that all colored salts contain elements from the heavy metal and rare earth groups, either as cation (e.g., Cu^{++}) or as anion (e.g., CrO_4^{--}).

The hydroxides of aluminum, zinc, lead, and a number of other heavy metals are **amphoteric** (Greek, *both*). This means that **such hydroxides possess both the properties of bases and of acids.** Zinc oxide, for example, readily dissolves in dilute sulfuric acid to form zinc sulfate, $ZnSO_4$ (which makes zinc oxide a base); and in sodium hydroxide to form sodium zincate, Na_2ZnO_2 (which makes it an acid anhydride).

415. Occurrence of the Metals.—The periodic table and the positions of the elements in the electrochemical series (§ 72) will help us to remember the forms in which the different metals occur in nature.

It is plainly only under unusual circumstances that a metal above hydrogen in the electrochemical series can exist in nature in the *free* or *native* condition, i.e., uncombined with other elements. For if such a metal were exposed to running water or to the moisture of the air, it would displace hydrogen and be itself converted into an oxide or hydroxide. Thus, the only metals commonly occurring native are copper, gold, silver, mercury; the members of the platinum group; and the members of the arsenic group.

Members of Group I*A* (called the **alkali metals**) occur in the complex silicate rocks and minerals, and in great deposits of soluble chlorides, sulfates, and carbonates. The important commercial sources of the other metals are, for the most part, insoluble compounds.

Summary of the Occurrence of the Metals

Group IA. Silicates; soluble chlorides, sulfates, carbonates.

Group IIA. Insoluble carbonates, sulfates, silicates.

Heavy metals below hydrogen in electrochemical series.—Native. Silver and copper occur also as sulfides.

Other heavy metals.—Insoluble oxides or hydroxides, sulfides, silicates, a few (Fe, Pb, Zn, Cu) as carbonates.

416. Metallurgy.—Whenever a mineral occurs in nature in sufficient quantity and purity to be useful **as a source of the metal concerned,** it is called an **ore.** The art of separating the metals from their ores, called **metallurgy,** had its beginnings long before there was any science of chemistry. The ancient Egyptians and Babylonians, and primitive peoples in all parts of the world, since prehistoric times, separated copper, iron and a few other metals from their ores by processes that were the same in principle as those in use to-day.

The metallurgical processes necessary in any given case will depend both on the nature of the ore and on the metal to be separated. The heavy metals are the easiest to separate, and about half a dozen of them were in common use long before written records were invented. The light metals, on the contrary, have been known only about a century: and the most remarkable of them, radium, was discovered within the present generation.

The metallurgical operations (often called **smelting operations**) employed in winning the heavy metals fall into four groups:

1. First the ore needs to be separated from useless foreign material, collectively known as **gangue,** with which it is commonly associated in nature (quartz rock, sand, clay, or limestone). This may be done by sifting, or by selection by hand, or by washing with a stream of water to carry away the lighter material. Sometimes the finely ground ore particles are floated off as a froth or foam, in the presence of a trace of oil (§ 529). Magnetic separation may be resorted to for removing Fe_3O_4. Such preliminary treatment of the ore is known as **concentration.**

2. After concentration, many ores need to be **roasted.** The process consists in heating the powdered ore in a current of furnace gases, mixed with an excess of air. Sulfur and arsenic are thus oxidized and carried away, and the ore is commonly converted into oxide:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

3. Following roasting comes **reduction** in a properly constructed furnace. The reducing agent is ordinarily coke or some other form of carbon, or carbon monoxide, produced by incomplete combustion of the carbon.

$$ZnO + CO = Zn + CO_2.$$

At the same time, a **flux** is commonly employed: namely, some substance of opposite chemical character to any gangue that may still remain in the ore. A silicious gangue will require a limestone flux, and *vice versa*. **Flux and gangue unite to form a fusible silicate slag** which floats on top of the molten metal collecting in the bottom of the furnace:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2.$$

In certain cases reduction is effected by metallic aluminum instead of carbon (thermite process, § 478):

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

4. Finally, the crude metal produced by reduction needs to be freed from small quantities of other metals, by a process of purification, or **refining.** In certain cases this is done by remelting with a properly chosen flux. Sometimes an electrolytic process is resorted to (§ 531). **The alkali and alkaline earth metals are prepared by electrolysis of their fused chlorides or hydroxides** (§§ 432, 448, 454).

417. Solubility of Metallic Salts.—The terms soluble and insoluble are, of course, only relative. Glass, quartz, and most other substances * considered as insoluble can be dissolved to a slight but measurable extent by prolonged boiling with water. Roughly, a substance that dissolves less than about 1 g. in 100 cc. is classified as slightly soluble; and one that dissolves less than about 0.01 g. in 100 cc. as insoluble.

The table on page 429, giving a rough survey of the relative solubilities of different salts should be committed to memory at once. Many practical applications will be found in what follows (§ 418).

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* Metals like gold, silver, copper, and platinum are not appreciably soluble. When they appear to dissolve in traces it seems likely that they are acted upon chemically to a very slight extent by the water, or by impurities dissolved in it.

	Soluble	*Insoluble.*
Acetates, chlorates, nitrates	All	None *
Chlorides, bromides, iodides	All, except	Ag, Hg′, Pb Tl′ †
Sulfates, chromates.......	All, except	Ag, Hg′, Pb, Ca, Sr, Ba
Sulfides.................	Groups IA, IIA	All others
Oxides, hydroxides, carbonates, oxalates, (borates, phosphates, silicates, fluorides)...............	Group IA	Nearly all others

Details will be found more accurately stated in the table facing the back cover. Notice that the salts of sodium, potassium, and ammonium are nearly all soluble (exceptions, § 441).

418. Preparation of Salts.—Review §§ 112, 138, 161. One who has passed through a course in general chemistry should be able to prepare many simple substances, on demand, from others. Skill in this very practical accomplishment comes only from practice in the laboratory, and is the characteristic that distinguishes one who really understands chemistry from one who has merely memorized facts about it. In the end, however, laboratory practice must be guided by a knowledge of general principles. The more thoroughly we understand these, the surer our progress in their practical applications.

An important group of laboratory methods are concerned with the preparation of salts. We usually start with (1) **a metal;** (2) **a base;** or (3) another **salt** containing the given metal. Any one of these three may react with (1) **a non-metal;** (2) **an acid, or acid anhydride;** or (3) **a salt** derived from a given acid. Thus there are nine different combinations, representing nine different principal methods for preparing salts—together with various other, special methods.

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* But there are a few insoluble basic acetates and nitrates.

† These are mercur*ous* and thall*ous* salts. Those of mercury and thallium in the higher valence (Hg″, Tl‴) are soluble. Cuprous chloride, CuCl, is insoluble, but is quickly oxidized and dissolved when exposed to the air. There are also a few insoluble basic chlorides (Sb, Bi, Sn, Pb).

	Metal	Base	Salt
Non-metal.	1	4	7
Acid......	2	5	8
		Double decomposition	
Salt..	3	6	9

1. **Direct union of metal and non-metal.** This method of forming salts is of the greatest service when the use of water has to be avoided to prevent hydrolysis (as in preparing anhydrous aluminum chloride). The more active the two elements the easier, as a rule, to bring them into combination.

With the help of the index, review reactions previously studied for the direct union of metals with fluorine, chlorine, bromine, iodine, nitrogen, and sulfur. Write equations for reactions which you find mentioned but not completely formulated.

Write equations for the preparation of calcium carbide, calcium phosphide, aluminum nitride.

2. **Dissolving a metal in an acid.** Review § 72. If the metal is active, any dilute, non-oxidizing acid of reasonable activity will commonly serve. The metallic atoms transfer electrons to hydrogen-ion, and the product is hydrogen gas. An inactive acid, however, will fail to dissolve the metal very rapidly; while if the metal is below hydrogen in the electrochemical series, it is usually necessary to use an oxidizing acid to dissolve it. In this case electrons are transferred to the anion of the oxidizing acid, and the latter is reduced (§ 302).

Write an ionic equation for the action of hot concentrated sulfuric acid on copper.

If a metal has two different valences (Fe, Sn, Cr) it commonly assumes the lower one (almost entirely), when it dissolves in a dilute, non-oxidizing acid.

How would you prepare stannous chloride from metallic tin, and how convert it into stannic chloride?

Write molecular equations for dissolving each of the following metals in dilute sulfuric acid, or explain why it will not dissolve: Al, Fe, Ag, Li. Rewrite these equations in ionic form.

3. **Action of a metal on the salt of another metal occupying a lower position in the electrochemical series (§ 422).** This displacement is commonly complete; though, if the two metals

(Sn, Pb) are very close together in the table of equilibrium potentials (Appendix G) it may remain incomplete.

Write molecular and ionic equations for the preparation, by this method, of ferrous acetate from silver acetate.

4. **Action of a base on a non-metal.** The most important examples are found among the halogens (§§ 184, 202).

Write molecular equations for good methods for preparing barium iodate, sodium chlorate, potassium hypochlorite.

Translate these equations into ionic form.

5. **Action of a base on an acid.** If the base and acid are both **active,** the reaction will be complete; otherwise there will be slight or complete hydrolysis (§ 113).

Write molecular equations for good methods for preparing zinc chloride, cuprous bromide, cupric bromide, lead acetate, ferric sulfate, aluminum nitrate, secondary sodium phosphate; ammonium oxalate, potassium bisulfate.

Write these same equations in ionic form (§268).

6. **Action of a base on a salt.** If the reaction is to be complete, the new base formed in this double decomposition must be **volatile, insoluble,** or very **slightly active.**

Write equations for the preparation of sodium sulfate from ferric sulfate and ammonium sulfate, respectively. Tell why the reaction is complete in each case.

7. **Action of a non-metal on a salt of a given metal.** The most important examples are among the halogens (displacement, § 200).

State the rule that determines which of two halogens will displace the other.

Show that the common method for preparing thiosulfates (§ 237) comes under this general heading.

8. **Action of an acid on a salt of a given metal.** If the double decomposition is to be complete, the same conditions must obtain as in (6). One of the products must be **volatile,** or **insoluble,** or **slightly active.** It is also commonly necessary that the acid used shall be **active** (§ 420).

$$NaNO_3 + \underset{\text{Active}}{H_2SO_4} \rightarrow NaHSO_4 + HNO_3 \uparrow .$$

$$HgNO_3 + \underset{\text{Active}}{HCl} \rightarrow HNO_3 + HgCl \downarrow .$$

$$NH_4C_2H_3O_2 + \underset{\text{Active}}{HCl} \rightarrow NH_4Cl + \underset{\text{Slightly active}}{HC_2H_3O_2}.$$

9. **Double decomposition between two salts.** If the reaction is to be complete, one of the new salts formed must be **insoluble.**

Starting with a nitrate of a different metal in each case, write and balance equations for the production, by this method, of an insoluble fluoride, chloride, bromide, iodide, sulfide, sulfate, carbonate, chromate, silicate, borate.

What other salt than the nitrate might have been used throughout the above reactions.

Write the above reactions in ionic form (§ 265).

Lithopone is an intimate mixture of zinc sulfide and barium sulfate. Tell how it may be made by a single double decomposition.

In a modification of this method, double decomposition takes place between fused salts at a high temperature. This is a method by which many minerals are formed in nature. Its chief use in the laboratory is in bringing insoluble salts or silicate minerals into solution. Thus, glass (approximately a metasilicate, § 406), when fused with an excess of sodium carbonate, is largely converted into calcium carbonate, which may easily be dissolved in dilute hydrochloric acid:

$$CaSiO_3+Na_2CO_3 \rightleftarrows CaCO_3+Na_2SiO_3,$$
$$CaCO_3+2HCl \rightarrow CaCl_2+H_2O+CO_2 \uparrow .$$

In carrying out such a fusion, a platinum crucible is commonly used, since glass or porcelain would react with the sodium carbonate. An excess of sodium carbonate is always used, for the reaction between the fused salts is reversible.

419. Ion-Product and Solubility-Product.—If a number of different kinds of ions are present together in the same solution, the utmost concentration that any one of them can attain is determined by the others. Thus, no very great concentration of Ag^+ can be present in a solution, in the presence of BrO_3^-, nor any very great concentration of BrO_3^- in the presence of Ag^+; for these two kinds of ions tend to separate together, taking up definite positions in space with respect to each other, to form crystals of the slightly soluble salt, silver bromate.

If such a precipitate is actually to appear in any given case, Ag^+ and BrO_3^- ions must be built into the crystal lattice (§ 95) at a rate more than sufficient to counterbalance the rate at which other ions, of the same kind, depart from it. In other words, the reaction by which the precipitate is produced must have at least a *certain minimum velocity.* Now, reaction velocity, in such a simple case, is very nearly proportional to the product of the concentrations of the reacting substances (§ 214). Accordingly, the product of the concentrations of Ag^+ and BrO_3^- must have a certain minimum value. Such a product of the concentrations of reacting ions, expressed in gram-ions * per liter, is called an **ion-product.** † The value which it has for a saturated solution of a given salt, is called the **solubility-product** for that salt.

Thus, the solubility of silver bromate is 0.006 mole per liter. A saturated solution of silver bromate will therefore contain 0.006 gram-ion of Ag^+, and 0.006 gram-ion of BrO_3^-; and the ion-product (which, for a saturated solution, is the same as the solubility-product) will be $0.006 \times 0.006 = 0.000036$.

In general, then, **two oppositely charged ions may be present in a solution together provided the ion-product does not exceed a certain figure, which is the solubility-product for that temperature. The moment the ion-product does exceed the solubility-product, the solution becomes supersaturated, and precipitation may or may not take place.**

In this course we shall be satisfied with this mere qualitative statement of the principle of the solubility-product, without attempting to apply it in calculating the actual solubility of one salt in the presence of another, when the two have some ion in common. Such calculations are based on the assumption that the solubility-product of a salt dissolving in pure water is not appreciably different from its value in the presence of small concentrations of other salts. This assumption seems warranted, so long as we deal only with slightly-soluble salts (such as $AgBrO_3$) that dissociate in such a way that each molecule furnishes two univalent ions. For salts furnishing divalent ions, and especially for those furnishing trivalent ions, electrical influences come into play, that tend to increase solubility, and results calculated with the help of the solubility-product principle may not be even approximately correct. On the other hand, any very large concentration of the added salt will often cause the solubility of the slightly soluble salt to become less than that calculated from the value of the solubility-product in pure water.

420. Precipitation.—Double decomposition, in terms of the ionic theory, consists in the direct union of oppositely charged ions to form a slightly soluble or slightly ionized substance (§ 138). Thus, when a solution of a soluble strontium salt is added to a solution of potassium chromate, a yellow precipitate of strontium chromate is produced:

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* A gram-ion is the weight in grams corresponding to the formula-weight of the given ion; 40 g. for Ca^{++}, and 96 g. for SO_4^{--}.

† If two or three ions of a given kind are needed to form a molecule of the given precipitate, the concentration of that particular kind of ion must be squared or cubed, in forming the ion-product.

$$Sr^{++} + CrO_4^{--} \rightarrow SrCrO_4 \downarrow$$

Nevertheless, strontium chromate is not entirely insoluble; and after the process of precipitation is complete, the solution still contains small concentrations of the ions Sr^{++} and CrO_4^{--}, in equilibrium with the precipitate.

Now if a little acid be added to the solution, we find that the precipitate dissolves. This is because the hydrogen-ion of the acid combines with the chromate-ion of the solution to form dichromate-ion:

$$2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{-} + H_2O.$$

The CrO_4^{--} thus removed from the solution of course tends to be replaced by the dissolving of a part of the precipitate; and if hydrogen-ion has been added in requisite concentration, the precipitate may dissolve completely. Otherwise expressed, chromate-ion may be so completely transformed into dichromate-ion that the ion-product (conc. of Sr^{++})×(conc. of CrO_4^{--}), becomes less than that necessary for a saturated solution.

In general, precipitation does not take place unless both of the substances furnishing the two ions of the precipitate are at least reasonably well ionized; for otherwise the product of the concentrations of the ions commonly fails to reach a sufficiently high value to permit a precipitate to appear. **Hydrogen sulfide is actually the only slightly ionized acid that may be used as a precipitating agent;** and it serves only for the production of a very few sulfides which happen to be so extremely insoluble that the merest trace of sulfide-ion occasions their precipitation.

To redissolve a precipitate, one of its two ions must commonly be made to combine with something else, and thus be put in reserve. For example, chromate-ion, in the previous example, was put in reserve as dichromate-ion, and thus caused the precipitate to dissolve. Again, calcium carbonate readily dissolves in the presence of carbonic acid (§153), since one of its two ions (CO_3^{--}) then combines with carbonic acid to form acid-carbonate ion, HCO_3^-.

Slightly soluble salts of slightly active acids are almost always readily dissolved by active acids. Thus ZnC_2O_4 and $Ca_3(PO_4)_2$, though insoluble in water, readily dissolve in the presence of HCl; for the ions $C_2O_4^{--}$ and PO_4^{---} then combine with H^+, and are thus put in reserve as molecules of the very moderately active acids, $H_2C_2O_4$ and H_3PO_4.

421. Double and Complex Salts.—Double salts, properly so called, are those that furnish the same ions, when dissolved in water, as their constituent salts would furnish separately. Thus, ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, sometimes written $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, is a double salt because it furnishes the ions NH_4^+, Fe^{++}, and SO_4^{--}. The alums (§ 479) are also typical double salts.

Complex salts, on the other hand, furnish different ions from those that their constituent salts would furnish separately. Thus potassium ferricyanide, $K_3Fe(CN)_6$, is a complex salt, rather than a double salt; because it does not furnish the simple ions K^+, Fe^{+++}, and CN^-, but rather K^+ and the complex ion, $Fe(CN)_6^{---}$ (called ferricyanide-ion).

Often the distinction between double and complex salts cannot be very sharply drawn, for the simple ions that are characteristic of double salts do sometimes combine, to a slight extent, to form complex ions; while the complex ions that are characteristic of complex salts are dissociated, to a very slight extent at least, into ordinary simple ions (see § 543).

Now, a precipitate separates from a solution only when the product of the concentrations of its constituent ions exceeds a certain value. This cannot happen if the concentration of one of these ions has been very much reduced, by its being withdrawn to form a complex ion. Thus, by adding NH_4OH to a solution containing Cu^{++}, we may withdraw most of the latter to form the complex copper-ammonia ion, $Cu(NH_3)_4^{++}$. In such a solution the concentration of Cu^{++} is so much reduced that a precipitate of $Cu(OH)_2$ is no longer formed on adding NaOH. Nevertheless, $(NH_4)_2S$ still brings down a precipitate of CuS, since this latter salt is so extremely insoluble that the merest trace of Cu^{++} is sufficient for its formation.

Similarly, by the addition of KCN to a solution of a silver salt, the complex salt $K \cdot Ag(CN_2)$ is formed (§ 543). Silver is thus put in reserve as the complex-ion, $Ag(CN)_2^-$; and, in the end, the concentration of Ag^+ is so much diminished that AgCl is no longer precipitated if we add a solution containing Cl^-.

EXERCISES

1. What is meant by the "order of increasing electropositive character"?

2. With the help of the periodic table arrange the following elements as nearly as you can in the order of increasing electropositive character. Fe, He, Zn, Ca, K, Au, Cl. What relation does your list bear to the electrochemical series?

3. Write formulas for such of the following compounds as you believe exist, and tell why you believe the others to be non-existent: boron hydride, selenium nitrate, molybdic acid, scandic acid, argon hydride, radium bromide, telluric acid, permanganic acid, rubidium fluoride, titanic chloride, cobaltic nitrate, boron acetate, nickelous hydroxide, telluric acid anhydride, zinc phosphate, phosphorus nitrate, arsenic sulfate.

4. What are some of the distinguishing properties of the heavy metals?

5. Indicate whether you consider each of the following substances to be (*a*) insoluble; (*b*) soluble, forming a base; (*c*) soluble, forming an acid; (*d*) soluble, ionized; (*e*) partially hydrolyzed; (*f*) completely hydrolyzed; (*g*) non-existent: MgO, Fe_2O_3, $As_2(CO_3)_3$, $CaCl_2$, PBr_3, $MnSO_4$, Na_2CO_3, $Si(NO_3)_4$.

6. Explain why aluminum is never found native.

7. Explain why galena is regarded as an ore, while phosphate rock is not.

8. What weight of coke is needed to reduce a metric ton (= 1000 kg.) of ore containing 60 per cent F_2O_3? How many cubic meters of carbon monoxide will be given off (§147)?

9. Look up the solubility of silver acetate, in grams per 100 cc. Recalculate this to moles per liter, and compare with the tabulated figure.

10. From the preceding data, calculate the solubility-product for silver acetate.

11. From the tabulated solubility of silver bromate, calculate the numerical value of its solubility-product, assuming complete dissociation.

12. The *solubility-product* of silver bromate in the presence of a slight concentration of another salt is assumed to be the same as it is in pure water. Determine what the concentration of Ag^+ must become in the presence of an excess of BrO_3^-, when the total concentration of BrO_3^- is 0.1 gram-ion per liter.

13. Barium chloride is treated separately with each of the following reagents: Na_2SO_4, H_2SO_4, H_2CO_3, Na_2CO_3, H_2S, Na_2S, HF, NaF. Write equations for such reactions as become practically complete. When practically nothing happens, tell why.

14. Explain, in general, how the precipitation of a salt may be made as complete as possible.

15. Discuss the conditions that must be fulfilled in redissolving a precipitate. Illustrate with two examples, explaining what is put in reserve, and in what form, in each case.

CHAPTER XXXII

ELECTROCHEMISTRY

422. How the Electrochemical Series is Extended to Include Oxidizing and Reducing Agents in General.—The electrochemical series, in its simplest form (§ 72), is a list of oxidizable substances (metals). Read from below upward, it gives the order of increasing ease of oxidation. • Metals nearest the top are the most readily oxidized, that is they part most readily with electrons to form cations:

$$Na \longrightarrow Na^{+} + e.$$

But our list may readily be extended, to include other oxidizable substances than the metals themselves, such as oxidizable cations (Fe^{++} and Sn^{++}). Moreover, certain anions are oxidizable, that is, may be made to part with electrons, and be discharged:

$$2Cl^{-} \longrightarrow Cl_2 \uparrow + 2e.$$

Oxidation results in a metal going into solution as a cation, or in the valence (+) of a cation being numerically increased; or it results in an anion being discharged from solution, or in its valence (−) being numerically decreased.

Our list of oxidizable substances, then, will be made up of **metals, oxidizable cations,** and a few common **anions.** These are **reducing agents.** Arranged, again, from below upward, in the order of *increasing ease of oxidation*, which is the order of *increasing activity as reducing agents*, we have the list given in the left-hand column of the table on the next page.

Similarly, in the middle column, we may prepare a list of *reducible* substances. These are merely the oxidized forms of the substances in the other list, and will therefore include **cations and uncombined non-metals.** These are **oxidizing agents.** Naturally, substances at the bottom of this new list, which were the hardest to produce by oxidation, will be the easiest to reduce.

In other words, this new list, read from above downward, gives the order of increasing ease of reduction, or the order of increasing activity as oxidizing agents.

Order of increasing ease of oxidation ↑ *or increasing activity as reducing agents*

Order of increasing ease of oxidation ↑ *or increasing activity as oxidizing agents*

Oxidizable substances (Reducing agents)		*Reducible substances (Oxidizing agents)*	*Potential (in volts)*
Li	⇄	$Li^+ + e$	+2.96
K	⇄	$K^+ + e$	+2.92
Na	⇄	$Na^+ + e$	+2.72
Mg	⇄	$Mg^{++} + 2e$	+1.55
Al	⇄	$Al^{+++} + 3e$	+1.35
Zn	⇄	$Zn^{++} + 2e$	+0.75
Fe	⇄	$Fe^{++} + 2e$	+0.45
Cd	⇄	$Cd^{++} + 2e$	+0.40
Ni	⇄	$Ni^{++} + 2e$	+0.21
Pb	⇄	$Pb^{++} + 2e$	+0.12
Sn	⇄	$Sn^{++} + 2e$	+0.13
H	⇄	$H^+ + e$	+0.00
Cu	⇄	$Cu^{++} + 2e$	−0.35
$4OH^-$	⇄	$O_2 + 2H_2O + 4e$	−0.40
$2I^-$	⇄	$I_2 + 2e$	−0.54
Fe^{++}	⇄	$Fe^{+++} + e$	−0.74
Ag	⇄	$Ag^+ + e$	−0.80
$NO + 2H_2O$	⇄	$NO_3^- + 4H^+ + 3e$	−0.95
$2Br^-$	⇄	$Br_2 + 2e$	−1.08
$2Cl^-$	⇄	$Cl_2 + 2e$	−1.35
$Mn^{++} + 4H_2O$	⇄	$MnO_4^- + 8H^+ + 5e$	−1.52

423. Application of the Electrochemical Series to Replacement Reactions, and to Oxidation and Reduction in General.—The electrochemical series, as just presented, gives an indication of whether any specified reaction of oxidation and reduction is possible or impossible. **If the reducing agent occupies a higher position in the table than the oxidizing agent, the reaction is possible, and under proper conditions may be expected to take place.** Thus Fe, in the list of reducing agents, occupies a much higher position than Cu^{++}, in the list of oxidizing agents. Thus we may expect Fe to reduce Cu^{++} to metallic copper:

$$Fe + Cu^{++} = Fe^{++} + Cu.$$

In other words, electrons are lost by the metallic iron, and transferred to copper ions, causing the latter to be deposited as metal. This is the ionic representation of a replacement reaction, otherwise formulated:

$$Fe + CuSO_4 = Cu + FeSO_4.$$

Similarly for other replacement reactions, and for oxidation and reduction in general. Ag, in the list of reducing agents, occupies a position above Cl_2, but below I_2, in the list of oxidizing agents. Thus Ag and Cl_2 combine directly to form AgCl; while Ag and I_2 do not combine directly.

Nevertheless, the series has several distinct limitations, which must be kept in mind:

1. **The positions of substances with respect to each other in the electrochemical series are not absolutely fixed, but are dependent on the temperature and on the concentration of the ions concerned.**—Increasing the concentration of an oxidizable ion makes it easier to oxidize; increasing that of a reducible ion makes it easier to reduce. Thus, by increasing the concentration of a solution of HCl, Cl^- is more readily oxidized to gaseous chlorine, at the anode; and H^+ more readily reduced to gaseous hydrogen.

2. **A substance sometimes appears to lose or gain electrons so slowly that other substances, less readily alterable, are given a chance to react.** Thus, a heavy current, passed through an acidified solution of $CuSO_4$, not only reduces Cu^{++} to Cu but even some H^+ to H_2; and this in spite of the fact that H^+ is less readily reducible than Cu^{++}.

3. **A catalyzer must often be present before a substance can be oxidized or reduced as readily as its position in the electrochemical series would indicate.** Thus, gaseous hydrogen (H_2) as a reducing agent, and hydrogen-ion (H^+) as an oxidizing agent, occupy the positions assigned to them only in the presence of finely divided platinum or palladium. This is the principle of the hydrogen electrode (§ 274).

Again, according to the electrochemical series, H_2 should reduce O_2, thus forming H^+ and OH^- (namely H_2O); but at room temperatures, in the absence of a proper catalyzer, the reaction is too slow to be perceptible.

Such examples make it very apparent that the electrochemical series indicates plainly when a reaction is *impossible;* but that a reaction which it shows to be *possible* may proceed at an inappreciable velocity.

424. How Chemical Reactions Produce Electric Currents.—Chemists have long believed chemical reactions to be of an electrical nature. Atoms of the same kind or of different kinds combine or part company because of the kinds or amounts of the electrical charges that they bear. Especially is this true of reactions of oxidation and reduction, which consist in the transfer of electrons (unit charges of negative electricity) from one atom or group of atoms to another (§ 131).

Now, if such a transfer of negative electricity does actually take place in every oxidation and reduction, we should be able to take advantage of it to produce an electric current. In principle, the thing is easy. Instead of allowing electrons to be transferred *directly* from one atom to another, we compel them to pass through a wire or other metallic conductor, on their way from the substance that loses them to the one that gains them. Thus we have "chemical action at a distance." The atoms or ions that lose electrons (or are **oxidized**) are definitely separated from those that gain electrons (or are **reduced**). Under such conditions, the energy that the chemical reaction would otherwise release as heat (§ 218) takes the form of electrical energy—a stream of electrons.

The conditions to be observed are well illustrated in the sketch on the opposite page. A long, U-shaped tube is filled with a conducting solution (say one of **sodium sulfate**). Two platinum wires, to serve as electrodes (§ 65) are then dipped into the ends of the tube, and connected with a galvanometer by copper wires. Under such conditions the needle of the galvanometer fails to move. If we now pour into the left-hand end of the tube a solution of **ferrous sulfate,** and into the right-hand one a solution of **bromine,** a current at once begins to flow. Ferrous ions (Fe^{++}) yield up electrons to the platinum wire that dips into the ferrous sulfate solution, and are thus converted into ferric ions (Fe^{+++}). These electrons pass through the connecting wire and galvanometer and are delivered at the surface of the other electrode, converting bromine molecules (Br_2) into bromide ions (Br^-).

$$\underbrace{Fe^{++} \longrightarrow 2Fe^{+++} + 2e}_{\text{Oxidation}} \qquad \underbrace{2e + Br_2 \longrightarrow 2Br^-}_{\text{Reduction}}.$$

As the current continues to flow, the chemical changes occurring around the electrodes are made evident by changes in color. Around the anode the greenish color of a solution of ferrous sulfate (i.e., Fe^{++} ions) gives place to the yellow color of a solution of ferric sulfate (i.e., Fe^{+++} ions); while around the cathode the red color of bromine slowly fades away, since the solution here comes to contain only the colorless ions (Na^+, Br^-, SO_4^{--}) of sodium sulfate and sodium bromide.

For the ferrous sulfate, in the preceding experiment, we may substitute any easily oxidizable substance, and for the bromine any easily reducible substance. The complete circuit of an **electrochemical cell**—arrangement for producing an electric current by means of a chemical reaction, or the reverse,—thus consists of:

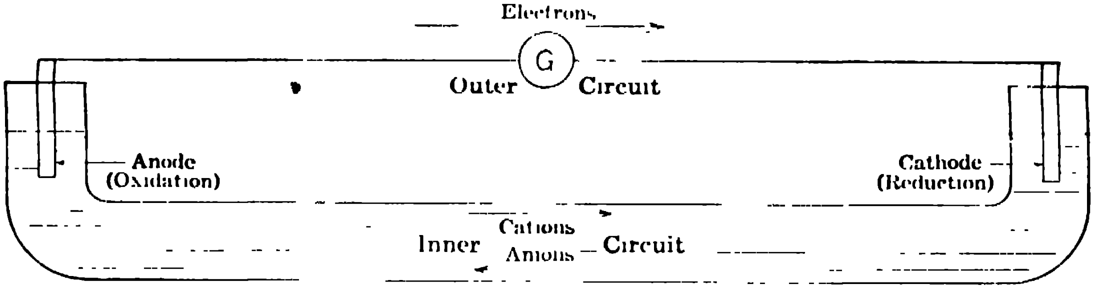

FIG. 98.1.—An electrochemical cell.

(*a*) A pair of **electrodes,** one (the **anode**) readily oxidizable, or in contact with readily oxidizable material; the other (the **cathode**) readily reducible, or in contact with readily reducible material.

(*b*) An **outer circuit,** consisting of a conductor (usually a metal) through which electrons are easily transferred from anode to cathode.

(*c*) An **inner circuit,** consisting of a solution of an acid, base, or salt, in an ionizing solvent (=polar solvent, § 252) or else of an acid, base, or salt in the molten condition. The ions of the dissolved or molten electrolyte migrate through this inner circuit while the current is passing, **anions** (negatively charged ions) in the direction of the anode, the **cations** (positively charged ions) in the direction of the cathode.

In producing an electric current by chemical means, it is very important that oxidation and reduction go on at separate places; for otherwise the electrons pass directly from the one substance to the other, and fail to traverse the outer circuit at all. Thus, if the ferrous sulfate and bromine, in the illustration just given, are mixed, they react, forming ferric ions (Fe^{+++}) and bromide ions (Br^-), just as before; but the galvanometer in the outer circuit shows no deflection, for all the energy of the chemical reaction is released in the inner circuit, as heat.

In the above sketch we assumed the anode and cathode solutions to be sufficiently far apart to prevent them from mixing. In other cases, they are of very different specific gravities, and remain for a long time in separate layers. In others, still, the anode solution is separated from the cathode solution by means of a jelly or a porous porcelain cup— anything, in fact, that will retard the process of mixing (due to diffusion), while permitting free passage for the ions, on their journey to anode or cathode.

425. Reactions at Anode and Cathode.—The **anode** is best defined as the electrode at which oxidation takes place, and the **cathode** as the electrode at which reduction takes place. This is true whether the given cell serves as a source of current (a primary cell) or whether it receives current from some outside source (an electrolytic cell, or a secondary cell, being charged) Actually, five different types of changes may occur at either electrode:

Anode	**Cathode**
The electrode at which substances yield up electrons to the outer circuit, or become oxidized.	**The electrode at which substances gain electrons from the outer circuit or become reduced.**
(*a*) Metallic atoms (often those of the anode itself) are oxidized to form cations:	(*a*) Cations are reduced to metallic atoms, and deposited on the cathode:
$Zn \rightarrow Zn^{++} + 2e.$	$Zn^{++} + 2e \rightarrow Zn$
(*b*) A cation, already present, is oxidized to a higher valence:	(*b*) A cation, already present, is reduced to a lower valence:
$Fe^{++} \rightarrow Fe^{+++} + e.$	$Fe^{+++} + e \rightarrow Fe^{++}$
(*c*) An anion is oxidized, losing its charge completely, and being separated as a non-metal:	(*c*) Non-metallic atoms are reduced, passing into solution as anions:
$2Cl^- \rightarrow Cl_2 + 2e.$	$Cl_2 + 2e \rightarrow 2Cl^-.$
(*d*) An anion is oxidized, losing its (negative) charge only in part:	(*d*) An anion is reduced, increasing its (negative) charge:
$\underset{\text{Sulfate ion}}{SO_4^{--}} \rightarrow \underset{\text{Persulfate ion}}{SO_4^{-}} + e.$	$SO_4^- + e \rightarrow SO_4^{--}.$

(*e*) Other chemical changes accompany the loss of electrons by an anion (§ 302):

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e.$$

(*e*) Other chemical changes accompany the gain of electrons by an anion:

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O.$$

426. Commercial Types of Cells.—In a **primary cell,** the oxidizable material composing or surrounding the anode and the reducible material composing and surrounding the cathode need to be renewed from time to time. In a **secondary cell (storage cell,** or **accumulator)** they may be restored, very largely, to their original condition, by sending an electric current through the cell in the opposite direction to that in which it passes during discharge. **In an ideal secondary cell, reversing the current completely reverses the chemical reactions taking place at anode and cathode.**

The right-hand column of the table of § 422 gives the potential, in volts (Appendix F), that a given reaction will set up, when the ion or ions concerned are present in a concentration of one gram-ion per liter. A plus sign means that the reaction that then tends to occur is one of oxidation. A minus sign means that the reaction that then tends to occur is one of reduction. The electrode composed of, or in contact with, the substance that is oxidized becomes the anode; and the one composed of, or in contact with, the substance that is reduced becomes the cathode. The actual electromotive force of any primary cell is approximately the algebraic difference between those set up at the two electrodes—with certain corrections that cannot be entered into here. The anode of the primary cell or secondary cell (during discharge) is commonly marked (−) and the cathode (+). The terminals of voltmeters and other measuring instruments are commonly marked with the sign of the cell electrodes to which they are intended to be connected.

The principal types of commercial primary and secondary cells are:

(*a*) **Weston primary cell.** The anode is an amalgam of cadmium and mercury; the anode solution a saturated solution of cadmium sulfate; the cathode solution, a saturated solution of cadmium sulfate and mercurous sulfate; the cathode, metallic mercury. The electromotive force of this cell (1.0183 volts at 20° C.) remains nearly constant with changing temperature. This feature makes the Weston cell an important standard, for determining the electromotive forces of other cells.

(*b*) **Dry cell.** In this primary cell the anode is zinc; the solution a paste of ammonium chloride in paper pulp, or some other convenient absorbent material; the cathode is a rod of carbon, packed in manganese dioxide. The latter serves as a **depolarizer,** a name given to any oxidizing agent used to free the cathode from hydrogen that may separate on its surface when too heavy a current is drawn through the cell.

(*c*) **Daniell cell.** In this primary cell, the anode is a rod of zinc; the anode solution a saturated solution of zinc sulfate; the cathode solution a saturated solution of copper sulfate; the cathode a plate of copper. Anode and cathode are commonly separated by a cup of porous porcelain. Though formerly of importance, this cell has been very largely displaced by the two following.

(*d*) The copper oxide-caustic soda (Lalande) cell is the most important primary cell with a fluid electrolyte. The cathode is a plate of compressed cupric oxide, the anode a plate of zinc, the electrolyte a solution of caustic soda. This cell will furnish heavy currents for long periods of time, without serious polarization.

(*e*) **Lead accumulator.** This, the principal storage cell, is discussed in § 579.

427. Electrolysis.—Metals and the few conducting non-metals (such as graphite) are often called "conductors of the first class." An electric current through such a substance consists of a stream of electrons, handed on from atom to atom; but in the end, each atom is left with the number of electrons that it had in the beginning, and the conducting substance is not permanently altered.

Solutions and molten electrolytes, on the other hand, often called "electrolytic conductors," or "conductors of the second class," are always chemically altered by the passage of the current, both at the place where electrons enter the electrolyte (cathode) and at the place where they leave (anode). An electric current through an electrolytic conductor consists of a stream of electrically charged particles of matter—the ions of the electrolyte. Though an electric impulse is conveyed through any conductor with the speed of light, the rate of motion of the ions themselves is not very great. Hydrogen ions, which are the speediest known, actually require five minutes to travel a distance of 1 cm., when urged forward by an electromotive force of 1 volt per centimeter (at room temperature).

As the ions arrive at the electrodes, they themselves, or other ions already present, are discharged. The clue to what will happen in any given case is furnished by the electrochemical series of § 422. **The principal reaction at the anode is the oxidation of the oxidizable element or ion nearest the top of the table.** In some cases this means that the anode itself is dissolved, to form cations; in other cases, that anions are discharged.

On the other hand, **the principal reaction at the cathode is the**

reduction of the reducible element or ion nearest the bottom of the table. In some cases this means that cations in contact with the cathode are reduced to a lower valence or deposited as metal; in other cases, that a non-metal in contact with the cathode is reduced to form anions (§ 126). In an elementary course it is sufficient to direct attention to the general conclusions that may be drawn with the aid of the table, without discussing individual details:

1. **If the anode is a metal above gold, it is usually oxidized and dissolved. If an "insoluble anode" is used** (gold, platinum, or carbon) **the anode product is usually oxygen** (formed by discharge of the hydroxyl ions of water or a base).

$$4OH^- \rightarrow 2H_2O + O_2 + 4e.$$

Chlorine, bromine, and especially iodine, may nevertheless be liberated at the anode by sufficiently heavy currents, from sufficiently concentrated solutions.

2. **If the solution to be electrolyzed contains no heavy metals, the cathode product is usually hydrogen.** Light metals (and aluminum) are deposited at the cathode (from aqueous solutions) only under very special circumstances (as when a very heavy current is used, with mercury present to dissolve the light metal as fast as it is separated, § 132).

3. **When solutions of salts of the heavy metals are electrolyzed, the heavy metal, in nearly all cases, is deposited on the cathode.**

4. **If there are several heavy metals present it is usually possible to deposit them in succession, beginning with the element nearest the bottom of the table, by gradually increasing the electromotive force applied to the cell.** This fact is of great importance in the electrolytic refining (purification by electrical means) of copper and other useful metals (§ 531). It is frequently used as a means of separating metals in chemical analysis. Thus, if an alloy containing silver, copper, and cadmium is dissolved in acid, the silver may be plated out on the cathode and weighed; then, by increasing the electromotive force, the copper; and, finally, the cadmium.

428. Faraday's Law.—Review §§ 148, 251. The table of equilibrium potentials, just discussed, determines what chemical changes take place at anode and cathode when an electric current is passed through an electrolyte, and what electromotive force is necessary in order to bring about a particular reaction.

However, it fails to tell us how much electricity must pass through an electrolyte in order to produce a given amount of chemical change at the electrodes—how much, for example, to liberate a thousand cubic feet of hydrogen, or prepare a pound of caustic soda, or purify a ton of copper. The question is an important one, for electrical energy costs money.

The quantity of electricity used in any electrolytic process is measured in coulombs, and is found by multiplying the current strength, in amperes, by the number of seconds during which the current flows (Appendix F). Thus, a current of 1 ampere, in one hour, will deliver 3600 coulombs through the circuit.

We have already noted that the quantity of electricity needed to chemically alter a gram-atom of any element at an electrode is proportional to the valence of that element (§ 251). In fact, **one gram-equivalent of material is chemically altered at each electrode for every 96,500 coulombs * passed through an electrolytic cell.** This is **Faraday's Law.**

One gram-equivalent of chlorine (atomic weight divided by valence) is 35.46 g.; of aluminum is $27.1 \div 3 = 9.03$ g.; of (cupric) copper is $63.57 \div 2 = 31.78$ g. Thus, on sending 96,500 coulombs through a solution of cupric chloride, 31.78 g. of copper will be liberated at the cathode, and, **at the same time,** 35.46 g. of chlorine at the anode. The same amount of electricity, passed through dilute sulfuric acid, will liberate 1.008 g. of hydrogen at the cathode, and 8 g. of oxygen at the anode (§ 127).

What weight of silver can be deposited from a silver nitrate solution by one coulomb of electricity? Ans. 0.001118 g.

How many seconds must a current of ten amperes flow in order to liberate 22.4 liters of chlorine gas, at standard conditions?

This is one gram-molecule, or two gram-equivalents, and will therefore require $2 \times 96{,}500 = 193{,}000$ coulombs, and will take a current of 10 amperes 19,300 seconds.

How strong a current must be passed through an electrolytic cell to separate one gram of copper in one hour?

One gram-equivalent, or 31.78 g. of copper, requires 96,500 coulombs. One gram will require proportionately less:

$\frac{1}{31.78} \times 96{,}500 = 3037$ coulombs, to be delivered in 3600 seconds. The current needed must accordingly be $3037 \div 3600 = 0.844$ ampere.

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* Sometimes 96,500 coulombs is called **one faraday.**

EXERCISES

422–427. 1. Explain what the electrochemical series has to do with the tendency of atoms to lose electrons. Illustrate.

2. Write ionic equations to represent the following changes:

Iron dissolving in an acid to form a ferrous salt.

A bromide being decomposed by gaseous chlorine.

A mercurous salt being oxidized to a mercuric salt by bromine.

3. Explain the three reactions just given as transfers of electrons.

4. What substance is liberated at the anode and what at the cathode, when an electric current is passed through each of the following: Fused KOH, dilute HCl, saturated KI, dilute H_3PO_4, dilute NaOH, dilute $NaNO_3$, dilute $HC_2H_3O_2$, saturated $CuBr_2$?

Write electronic equations for the changes at anode and cathode, in each case.

5. State the rule that determines the order in which several metals present in solution are deposited by electrolysis.

6. Describing the electrolysis of a dilute solution of sodium chloride a certain textbook reads: "The sodium ions move with the current toward the cathode, and are there discharged, forming metallic sodium. But this in turn reacts with the water of the solution and forms sodium hydroxide, with the liberation of free hydrogen." Defend or attack this statement with the help of the electrochemical series.

7. Read § 531. The principal metallic impurities in impure copper are Au, Ag, Pb, Zn, Fe. The first two of these remain in metallic form, and subside as "anode mud" when the copper goes into solution at the anode, during electrolytic refining. The other three metals go into solution along with the copper, but fail to come out again upon the cathode. Explain, with the help of the electrochemical series.

8. Explain how the conduction of an electric current through a wire differs from its conduction through a solution.

9. From the table of § 422 determine what will happen, if anything, when:

(*a*) A strip of lead is dipped into normal $AgNO_3$ solution.

(*b*) A strip of Sn into normal $FeCl_3$.

(*c*) A strip of Sn into normal HCl.

(*d*) When solid iodine is shaken with normal KBr.

(*e*) Gaseous chlorine is passed into normal KI.

Write ionic equations for the reactions that occur, and explain as transfers of electrons.

10. How can you justify the description of hydrogen as an oxidizable substance, and hydrogen-ion as a reducible substance, in terms of the electronic theory?

11. Give equations, in terms of the ions of water, to explain why the solution becomes alkaline in the neighborhood of the cathode, in the electrolysis of a solution of NaCl.

12. Under what conditions may oxidation and reduction reactions be made to yield an electric current. Tell how you would arrange to get a current from the reactions:

$$Cd+Cu^{++}=Cd^{++}+Cu.$$
$$Zn+Cl_2=Zn^{++}+2Cl^-.$$

13. Will the cadmium be anode or cathode in the first of the two preceding cells? Estimate the total electromotive force of this cell, under certain stated

concentrations. Tell whether an increase in the concentration of each ion will increase or decrease the electromotive force of the cell.

428. 14. Chromic sulfate is to be changed into sodium chromate by means of an electric current. Will it be placed in contact with anode or cathode? Why? From the change in valence and Faraday's Law calculate the number of ampere hours needed for each kilogram of sodium chromate produced, assuming perfect efficiency.

15. A silver plating bath and a copper plating bath ($CuSO_4$) are connected in series. How much copper will be deposited for every 100 mg. of silver?

16. It is proposed to prepare a standard solution of sulfuric acid by electrodepositing copper from a solution of copper sulfate. Write electronic equations for the chemical changes taking place at the two electrodes.

17. In the preceding question, how many milligrams of copper will be deposited for each cubic centimeter of N/10 acid produced? How many coulombs will this require?

18. How many coulombs of electricity are needed to liberate 672 cc. of mixed hydrogen and oxygen gases in the electrolysis of water, at standard conditions?

CHAPTER XXXIII

THE ALKALI METALS AND THEIR COMPOUNDS

429. Occurrence.—Salts of the two most important alkali metals (sodium and potassium) are widely distributed and very abundant; all the igneous rocks of the earth's crust contain small amounts. When these rocks weather, sodium and potassium find their way into the soil, the sodium salts to be extracted by running water and carried away to the ocean, the potassium salts to be withdrawn by growing plants. The ocean contains about 2.8 per cent $NaCl$ and 0.08 per cent KCl. The great natural deposits of sodium and potassium salts have been described elsewhere (§§ 176, 442).

An interesting fact is that **though igneous rocks contain sodium and potassium in very nearly equal amounts, sodium salts are more readily leached from the soil than potassium salts** (zeolites, § 408) and are found in the ocean in a much larger quantity. As the result of an adaptation to this situation, land plants have come to depend on potassium salts for their growth; while marine plants make liberal use of sodium.

430. Discovery of the Alkali Metals.—The substances we now call sodium hydroxide and potassium hydroxide were for a long time considered to be elements, for they resisted all attempts to decompose them by heat or chemical reagents. But Sir Humphry Davy, in 1807, in a series of brilliant experiments, succeeded in isolating the metals themselves.

The apparatus he used was a very simple one. Solid sodium hydroxide was melted in a platinum spoon. On passing an electric current through the liquid, from the spoon (anode) to a platinum wire (cathode) bright metallic globules of sodium and potassium appeared about the wire, and presently caught fire. This was the first time the two elements themselves had ever been seen, in spite of the fact that many of their salts had been known since prehistoric times. About half a century later the three other less abundant alkali metals were prepared by Bunsen, by similar methods.

431. Properties of the Alkali Metals.—

GROUP IA OF PERIODIC TABLE.

	At. Wt.	Density.	M. P.	B.	Spectrum Lines (§ 445).
Li. . . .	6.94	0.534	186°	1400°	Bright red
Na . . .	23.00	0.971	97°	877°	Yellow
K . .	39.10	0.862	62.5°	758°	Red-violet
Rb .	85.45	1.532	38.5°	696°	Dark red
Cs. . . .	132.81	1.87	26.4°	670°	Blue

The physical properties of the alkali metals are shown in the above table. The first three are lighter than water—lithium lighter in fact than most kinds of wood. The densities are roughly parallel to the atomic weights, but the melting points and the boiling points fall off as the atomic weights increase.

In chemical properties the alkali metals are very much alike. **They oxidize readily in contact with moist air,** and must therefore be preserved under the surface of some inert liquid, such as kerosene. **They decompose water very violently, forming strongly alkaline solutions (bases) and liberating hydrogen.** The activity of these bases increases with increasing atomic weight, being greatest for cesium hydroxide. Almost all the salts of the alkali metals are soluble.

432. Preparation of the Alkali Metals.—At the present time **both sodium and potassium are prepared by electrolysis of an electrolyte prepared by melting down the solid hydroxide,** at a temperature sufficiently high to expel water.

The electrolyte is largely ionized at the temperature required to melt it (§ 253).

$$\begin{array}{l} NaOH \rightleftarrows Na^+ + OH^- \\ \qquad\qquad\qquad\quad \updownarrow \\ \qquad\qquad\qquad H^+ + O^{--} \end{array}$$

The ions present are, accordingly, chiefly Na^+ and OH^-, with smaller concentrations of H^+ and O^{--}. On passing a current the positive ions (cations) migrate toward the cathode and are there discharged, producing metallic sodium and hydrogen gas:

$$2H^+ + 2e = H_2; \qquad 2Na^+ + 2e = 2Na.$$

The negative ions (anions) migrate toward the anode, and are discharged, producing oxygen gas:

$$4OH^- = 2H_2O + O_2 + 4e.$$

Sodium can also be prepared by the electrolysis of fused NaCl. But the process requires a higher temperature than is needed to melt NaOH, and there are other practical difficulties that interfere with its commercial usefulness.

433. The Castner Cell.—The apparatus devised by Castner and in use at Niagara Falls for the manufacture of metallic sodium and potassium is shown in Fig. 99. The cathode is an iron rod, introduced through the bottom of the cylindrical iron vessel which forms the cell, and held in place by fused sodium hydroxide, which is poured in around it and allowed to solidify. The anodes are iron rods surrounding the cathode, and separated from it by a cylinder of iron gauze. The electrolyte in the upper part of the vessel is first melted by a ring of burners; but after the electrolysis is under way, the heat liberated by the passage of the current is sufficient to keep the electrolyte in a fluid condition. The oxygen liberated outside the cylinder of iron gauze escapes through openings in the cover plate. Hydrogen and sodium, liberated within the cylinder, rise to the surface and collect inside the receptacle (*R*). The hydrogen escapes by lifting the iron lid of the receptacle, and the sodium is skimmed or ladled off from time to time.

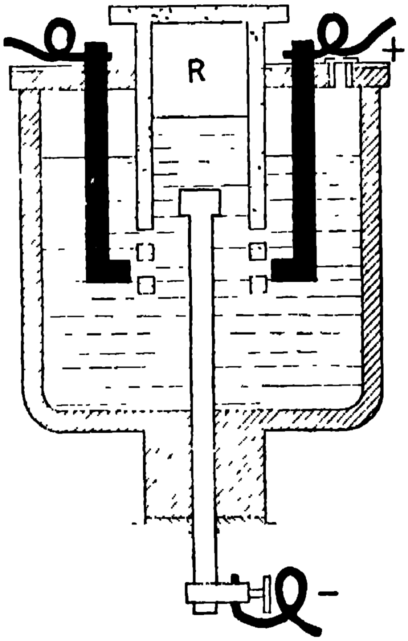

FIG. 99.—The Castner cell for manufacture of sodium by electrolysis of fused sodium hydroxide

434. Uses of the Alkali Metals.—Most of the metallic sodium now manufactured is converted into **sodium peroxide, Na_2O_2,** a yellow powder, by heating in aluminum trays at 400° C. in a current of air. **Sodium peroxide is an important oxidizing agent,** used commercially for preparing hydrogen peroxide for bleaching hair, silk, or other materials which would be injured by chlorine:

$$Na_2O_2+2HCl=2NaCl+H_2O_2.$$

Even an unacidified solution of sodium peroxide is thus hydrolyzed to sodium hydroxide and hydrogen peroxide. But if the solution is heated, or if a catalyzer is present, oxygen is liberated (§ 51). If sodium peroxide is heated with easily oxidizable material, an explosion may take place; nevertheless, in the presence of a large amount of inert material, such as sodium carbonate, the reaction is sufficiently moderated to be safe. Sodium peroxide is a rather dangerous laboratory reagent. It should never be added to hot water (51); and samples left in contact with paper are apt to start fires.

Metallic sodium is also an indispensable reagent in the preparation of a number of important organic compounds – dyes, medicinal substances, and perfumes. Alloyed with mercury (**sodium amalgam**), it is **an important reducing agent.** Metallic potassium is more expensive and more difficult to prepare than sodium, and at present has no important use for which sodium will not serve as well.

Sodium reacts with ammonia to form sodamide, $NaNH_2$, a crystalline compound which is of great industrial use in the synthesis of indigo (§ 377).

435. Preparation of the Caustic Alkalies.—Sodium and potassium hydroxides are known as **caustic alkalies,** or **lye.** They are deliquescent white solids, corrosive to the skin, and very soluble in water. They are prepared commercially by three distinct processes:

1. By treating a solution of sodium and potassium carbonates with slaked lime:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 \downarrow + 2NaOH.$$

This process, called **causticizing,** has been in use since the beginning of historic times. The precipitated calcium carbonate is filtered off; and the filtrate, containing sodium hydroxide or potassium hydroxide, is concentrated in evaporators, or used directly in the manufacture of soap (§ 363) or paper pulp (§ 371).

2. By the **Le Blanc process.** When sodium sulfate, prepared from common salt (§ 154), is heated with coke and limestone in a rotary furnace, it is reduced to sodium sulfide. This then reacts with the limestone to form sodium carbonate:

$$Na_2SO_4 + 4C = Na_2S + 4CO \uparrow .$$

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The product is a mixture of calcium sulfide and sodium carbonate, containing an excess of calcium oxide and carbon. It is extracted with water, when the sodium carbonate is decomposed by the excess of lime, giving sodium hydroxide:

$$Na_2CO_3 + CaO + H_2O = CaCO_3 \downarrow + 2NaOH.$$

For almost a century this process was the most important method for the preparation of sodium carbonate, but is now useful only as a source of sodium hydroxide and potassium carbonate.

3. By **electrolysis of solutions of sodium and potassium chlorides.** Chlorine and hydrogen are by-products of this process (§ 181):

$$2NaCl+2HOH=2NaOH+H_2\uparrow+Cl_2\uparrow.$$

One of the chief difficulties in the preparation of caustic soda by electrolysis is in keeping the chlorine and alkali from reacting to form sodium hypochlorite. In some of the most successful cells the chlorine and alkali are kept apart by the use of diaphragms of asbestos cloth (§ 181). But a product is obtained which is freer from unchanged sodium chloride if the anode and cathode compartments are separated by a non-conducting wall, dipping into a trough of metallic mercury.

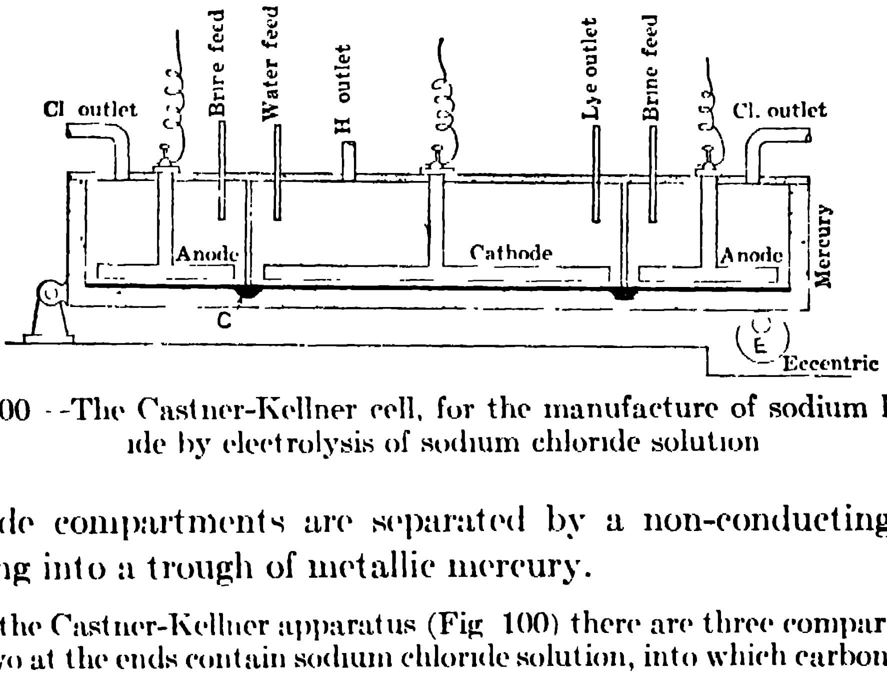

FIG 100 --The Castner-Kellner cell, for the manufacture of sodium hydroxide by electrolysis of sodium chloride solution

In the Castner-Kellner apparatus (Fig 100) there are three compartments. The two at the ends contain sodium chloride solution, into which carbon anodes dip The cathode is a layer of metallic mercury on the floor of the cell With concentrated solutions and heavy currents, there is separated at the cathode not only hydrogen but *metallic sodium* (§ 424). The latter alloys with the mercury to form a fluid amalgam (§ 561). The cell is constantly rocked by an eccentric (E), the amalgam being thus caused to flow under a partition into the central compartment There it is made to interact with water by being made anode in contact with a solution of caustic alkali.

436. Uses of the Caustic Alkalies.— The most important uses of the caustic alkalies are the refining of petroleum (§ 343) and vegetable oils, the mercerizing of cotton (§ 370), the manufacture of artificial silk (§ 370), the preparation of paper pulp (§ 371), the manufacture of soap (§ 363), hypochlorites (§ 205), chlorates (§ 206), and nitrites (§ 296). These uses together probably consume several hundred thousand tons of sodium hydroxide each year, and a smaller quantity of potassium hydroxide. A mixture of solid sodium hydroxide and solid calcium oxide, known as **soda-lime,** is used in the laboratory as an absorbent for carbon dioxide.

437. Occurrence and Preparation of Sodium Carbonate.—Both sodium carbonate and bicarbonate exist in nature in many of the drier regions of the world, the two most extensive deposits being Owens Lake, California, and Lake Magadi, in British East Africa. The former of these is estimated to contain not less than 50,000,000 tons of sodium carbonate, and the latter several times that quantity.

But in spite of the existence of these natural deposits, most of the sodium carbonate used in the industries is now prepared by the Solvay process. This is carried out in two stages:

(1) A strong solution of brine is saturated with ammonia and carbon dioxide gases. Sodium bicarbonate is precipitated:

$$\begin{array}{rcl}
NH_3+H_2O \rightleftarrows & NH_4OH & \\
 & + & \\
CO_2+H_2O \rightleftarrows & H_2CO_3 & \\
 & \upharpoonleft\downharpoonright & \\
NaCl+ & NH_4HCO_3 & \rightleftarrows NaHCO_3 \downarrow \; + NH_4Cl \\
 & + & \\
 & H_2O &
\end{array}$$

(2) Next the sodium bicarbonate is heated to redness, when it is decomposed, forming sodium carbonate:

$$2NaHCO_3 = Na_2CO_3 + CO_2 \uparrow \; + H_2O \uparrow .$$

The by-product of this process is ammonium chloride, which is distilled with slaked lime, to recover ammonia. (Write equation.)

438. The Chemical Industries.—The manufacture of glass, and other industries, probably consume more than 3,000,000 tons of sodium carbonate each year. Most of this tremendous total is produced by the Solvay process (§ 437) which has been able to restrict its rival, the Le Blanc process (§ 435), to the production of potassium carbonate and an impure grade of sodium hydroxide. The story of how this came to be is an instructive example of how the industrial chemistry of to-day is molded by the interplay of economic forces.

The Le Blanc process, depending for its existence on cheap sulfuric acid, was a great stimulus to the chamber process for the manufacture of sulfuric acid, and this in turn to the development of nitric acid (§ 297), superphosphate (§ 314), and the dyestuff industries (§ 372). Incidentally it produced hydrochloric acid as a by-product, which was oxidized commercially to chlorine (Deacon process, § 180), and thus led to the production of bleaching powder (§ 204) on a tremendous scale. Methods were furthermore developed for reconverting a second by-product of the Le Blanc process, calcium sulfide, into sulfuric acid, to be used over again. Thus a great group of interrelated industries, centering in Le Blanc soda, were built up during the first seventy years of the nineteenth century.

But during the half century just passed important new economic forces have come into existence. Cheap recovery of ammonia in the distillation of coal (§ 283) made possible the Solvay process, which was found to produce a purer grade of soda than had ever before been made commercially. Then the electrolytic caustic soda process (§ 181) produced so much chlorine that the Deacon process was superseded.

Thus much of the demand for hydrochloric acid, the chief by-product of the Le Blanc process, was cut off. The opening of great new deposits of sulfur (§ 225) and of sulfide minerals (§ 224) made it unprofitable to reconvert the other product of the Le Blanc process into sulfuric acid.

Thus, at the present time, the great chemical industries have fallen into an entirely new grouping. Nitrogen, from liquid air (§ 27) meets calcium carbide from electric furnaces for the synthesis of ammonia by the cyanamide process (§ 284); or nitrogen and hydrogen from the action of steam and air on coke form ammonia by direct synthesis. Closely related are the liquid chlorine industry (§ 181), which is tending to drive bleaching powder from the market; and the manufacture of dyestuffs and synthetic drugs. We also have the soap, glass, and paper industries, dependent on chlorine and caustic soda.

It is thus very clear that the great chemical industries, representing billions of dollars of invested capital, are in a state of *economic equilibrium*. New discoveries or economies in one field affect all the rest. Processes of commercial value to-day may need to be reversed to-morrow, in order to meet new economic conditions. But the well-established *principles* of chemistry remain. The Deacon process for the manufacture of chlorine (§ 180) is now almost extinct; but its basis, the law of mass action (§ 217), still holds. Aluminum is no longer reduced from its ores by metallic sodium; but the thermo-chemical principles that governed that reaction now find useful application in other directions. Processes dimly visioned yesterday are the established practice of to-day; and to-morrow in their turn may be overthrown.

The chemical discoveries of greatest industrial significance are accordingly not those that happen to find momentary practical application, but rather those that teach us more about general principles. By becoming familiar with these we turn our faces toward the future rather than the past.

439. Uses of Sodium Carbonate.—Anhydrous sodium carbonate is commonly called **soda,**[*] or **soda ash.** The hydrated salt

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[*] The word soda is also applied to Na_2O, as a hypothetical constituent of the silicates (§ 398) and other salts.

$Na_2CO_3 \cdot 10H_2O$ is referred to as **washing soda, sal-soda, or soda-crystals.**

The chief uses of sodium carbonate depend on three different properties:

(1) Since **carbonic acid anhydride, CO_2, is volatile,** the salt Na_2CO_3 may be used instead of the base NaOH for preparing the salts of other acids, by neutralization or by direct union with acid anhydrides:

Examples:

(*a*) Preparation of sodium acid sulfite:

$$Na_2CO_3+H_2O+2SO_2=2NaHSO_3+CO_2\uparrow.$$

(*b*) Preparation of glass (§ 406) and water-glass (§ 405):

$$Na_2CO_3+xSiO_2=Na_2O\cdot xSiO_2+CO_2\uparrow.$$

(*c*) In general in the industries whenever an acid needs to be neutralized, provided the escape of CO_2 offers no inconvenience.

(2) Na_2CO_3 is slightly hydrolyzed by water, liberating NaOH:

$$Na_2CO_3+HOH \rightleftarrows NaHCO_3+NaOH.$$

Sodium carbonate is accordingly useful in washing powders and other preparations the purpose of which is to impart a definite slight alkalinity to water. Of course NaOH would serve, but Na_2CO_3 is cheaper, and has the advantage of having reserve alkalinity, available for neutralization of acids, without the inconvenient caustic properties of NaOH.

(3) Since the carbonates of all the heavy metals are insoluble in water, Na_2CO_3 may be used to precipitate them. The most important case is the removal of objectionable calcium salts from water (water-softening, § 460):

$$CaCl_2+Na_2CO_3=CaCO_3\downarrow+2NaCl.$$

440. Sodium Bicarbonate.—Sodium bicarbonate, $NaHCO_3$, sometimes called *baking soda* or saleratus, is used as a substitute for yeast in preparing biscuits, being decomposed by heat with the liberation of CO_2, which distends and lightens the dough. *Ammonium bicarbonate*, NH_4HCO_3, is even better, since all the products of its decomposition are volatile, and is used on a large scale in the preparation of crackers. Baking powder usually contains $NaHCO_3$, together with an organic acid, monosodium phosphate, or alum (§ 479). It has the advantage over Na_2CO_3 of liberating twice as much CO_2 for each gram of solid residue left behind in the bread. Moreover, Na_2CO_3 is too alkaline (hydrolysis) to be used in food or in medicine.

441. Other Sodium Salts.- The properties and uses of a number of other important sodium salts are discussed elsewhere: fluoride (§ 209); hypochlorite (§ 205); chlorate (§ 206); perchlorate (§ 206); bromide (§ 209); iodide (§ 209); sulfite (§ 236); thiosulfate (§ 237); nitrite (§ 296); nitrate (§ 279); acetate (§ 105); cyanide (§ 338); silicate (§ 405); tetraborate (§ 412); phosphate (§ 313); chromate (§ 510).

As an exercise, tell how each of these salts may be prepared from sodium carbonate. Write equations.
State one important industrial use of each of these salts.

442. Natural Sources of Potash.—Most of the potassium salts of commerce are derived from great deposits in southern Germany (Stassfurt) and in France (Alsace). Here, in prehistoric times, great inland seas existed, which by slow evaporation deposited their dissolved salts in the order of increasing solubility—first calcium sulfate, then sodium chloride, then mixed potash and magnesium salts. In places the chloride layer is a thousand feet thick, and the mixed potash and magnesium salts over a hundred feet thick.

A great many double and triple salts, of somewhat complicated formulas, have been identified in these deposits. But most important by far is **carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$.** This, by a process of recrystallization, can be made to yield pure KCl, which is the starting point for the manufacture of all the other commercially valuable potassium salts.

These natural deposits have yielded rapidly increasing quantities of potash salts since their discovery almost a century ago. At the outbreak of the Great War, in 1914, the production of material of different grades amounted to almost 10,000,000 tons a year. Most of this went into fertilizers; for potassium, like nitrogen and phosphorus, is an element necessary to the growth of plants but often found in deficient quantity in the soil.

Of recent years a careful search has been made for potash within the United States. The most important of the several sources of supply now available are:

(1) *The salt lakes of California and Western Nevada.* Of these deposits the only one operating (1922) in competition with European potash is that of Searles Lake, California.

(2) *The fumes from cement kilns* (§ 465) are now often precipitated by the *Cottrell electrical precipitation process.* Electrical conductors, charged at high tension, are placed in the path of the fumes. The suspended particles

of dust become charged, and are repelled against the surface of a metallic plate, where they are deposited.

(3) *Plant ashes and sugar beet molasses*, which yields about 5 per cent K_2CO_3 when carbonized and extracted with water. The total amount of potash available from this source is insignificant in comparison with the needs of the country.

(4) The *kelp beds* of the Pacific Coast. A large plant near San Diego is no longer operated, apparently for lack of a market for by-products.

(5) Various *silicate minerals* (e.g., *leucite*) containing potassium. The supplies of these are inexhaustible, but none of the methods proposed for obtaining potash from them in soluble form has yet proved economically successful.

443. Potassium Carbonate.—Next to KCl, so easily prepared from carnallite (§ 442), the most important potassium salt is the carbonate K_2CO_3. This may be obtained by leaching plant ashes; but most of it is prepared by the Le Blanc process, very nearly as previously outlined for NaOH. The reactions of the first stage (§ 435) are:

$$KCl + H_2SO_4 = KHSO_4 + HCl;$$
$$KHSO_4 + KCl = K_2SO_4 + HCl.$$

The potassium sulfate is then ignited in a rotary furnace in the presence of coke and limestone:

$$K_2SO_4 + 4C = K_2S + 4CO$$
$$K_2S + CaCO_3 = K_2CO_3 + CaS.$$

The K_2CO_3 is leached out, and recovered by crystallization.

Potassium carbonate cannot be made by the Solvay process, by way of $KHCO_3$; for the latter salt, unlike $NaHCO_3$, is readily soluble in water and the reaction by which it might otherwise be formed (§ 437) is therefore incomplete:

$$KCl + \underbrace{NH_3 + CO_2 + H_2O}_{NH_4HCO_3} \rightleftarrows KHCO_3 + NH_4Cl.$$

Potassium carbonate is used in the preparation of soft soaps (§ 363), hard glass (§ 408), and in washing wool preparatory to dyeing.

Other salts are prepared from K_2CO_3 (or KCl) by the same methods as the corresponding sodium salts and have the same uses. They crystallize more readily than sodium salts and are therefore prepared in a somewhat purer form. But whenever the highest degree of purity is unnecessary, the cheaper sodium salts are always employed.

Tell how each of the following might be prepared, in one or several steps, from KCl; from K_2CO_3:

$$KOH,\ KClO,\ KClO_3,\ K_2SO_4,\ KNO_3,\ K_2S,\ K_2S_2O_3.$$

Write and balance equations for these reactions.

444. Analytical Tests for the Alkali Metals.—All compounds of the alkali metals are **colorless,** except the chromates, permanganates, and similar salts, owing their color to some particular nonmetallic radical. Accordingly **there are no analytical tests for the alkali metals that depend upon changes in color.**

The ready solubility of most of the salts of the alkalies furthermore makes it difficult to separate and identify these elements by precipitation. Nevertheless **potassium is frequently precipitated as the *perchlorate*, *chloroplatinate*, or *cobaltinitrite*,** commonly in the presence of alcohol (but perchloric acid, heated with alcohol, will oxidize the latter, *explosively*):

$$KCl + HClO_4 = \underset{\text{(White)}}{KClO_4} \downarrow + HCl.$$

$$2KCl + \underset{\substack{\text{Chloroplatinic} \\ \text{acid (§603)}}}{H_2PtCl_6} = \underset{\substack{\text{(Yellow)} \\ \text{Pot chloroplatinate}}}{K_2PtCl_6} \downarrow + 2HCl.$$

$$2KCl + Na_3Co(NO_2)_6 = \underset{\substack{\text{(Yellow)} \\ \text{Pot cobaltinitrite}}}{K_2NaCo(NO_2)_6} \downarrow + 2NaCl.$$

For a rough qualitative test, potassium may also be precipitated as the acid tartrate, $KHC_4H_4O_6$, fluoboride, KBF_4, or fluosilicate, K_2SiF_6; and sodium as the acid pyroantimonate, $Na_2H_2Sb_2O_7$.

Very small quantities of the alkali metals are best detected by a flame or spectroscopic test, next described.

445. The Spectroscope.—If a platinum or nichrome wire is dipped into a solution of a sodium salt, and introduced into the lower portion of a Bunsen flame, the latter will be colored yellow. Potassium salts color the flame reddish-violet, and lithium salts color it a brilliant carmine. It is easy enough to identify these and many other elements by this simple **flame test,** provided they are not present in admixture with each other. But in practical work it is precisely such mixtures with which we most frequently have to deal; and the brilliant yellow of the sodium flame will generally cover up the violet color due to small accompanying amounts of potassium.

If the flame is viewed through a square of blue glass, this will cut off the yellow rays and let the violet pass through, permitting the potassium to be recognized after all. (If ammonium salts are present they must first be removed by heating the material to redness. The residue is then redissolved in a few drops of dilute

HCl.) But other combinations cannot be dealt with in such a simple way. We use instead an instrument called a **spectroscope,** which sorts out the different tints that are blended in colored flames, and enables us to view them separately.

Fig. 101 shows a common type of spectroscope. Light from a colored flame, *F*, passes through a narrow slit, *S*, thence through a set of lenses contained in the tube *C*, to render the rays parallel. The beam next passes through a prism, *P*, made of heavy glass. Here it is refracted or bent aside. But the important point is that *the different kinds of light that go to make up the colored beam are bent aside to different degrees, and emerge from the prism in different directions.*

If some sodium chloride is introduced into the flame, then on swinging the telescope, *T*, from left to right about the prism as a center, we presently find a vertical yellow line, in reality a magnified image of the slit, *S*. This line is due to *sodium*. It has been observed when as little as one-millionth of a milligram of the element was present!

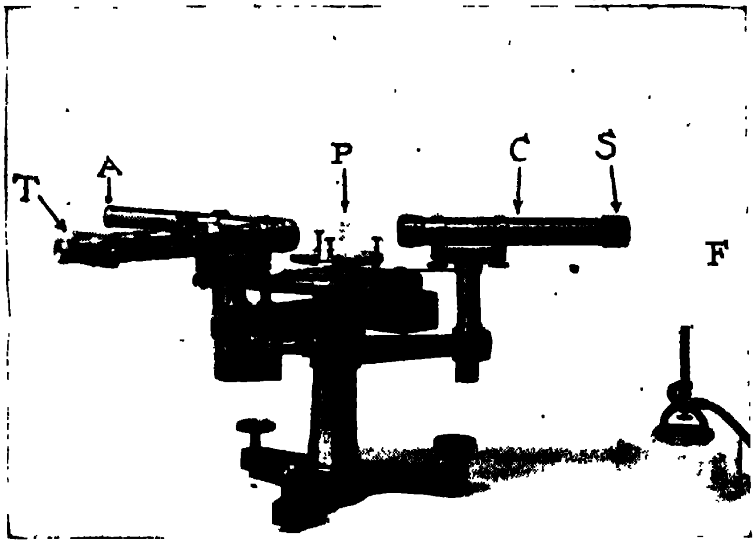

FIG 101 —A spectroscope The small tube, *A*, is for throwing an image of a graduated scale against the surface of the prism, to aid in identifying the spectral lines

If some potassium salt is now introduced into the flame, and the telescope swung a short distance to the left of the yellow line, we find a pair of red lines; and far away toward the right a faint, dark-violet line. All three of these are due to *potassium*, and would have been furnished by any salt of that element sufficiently volatile to color the flame. They always appear in definite positions with respect to each other and to the spectral lines of other elements.

It is well to notice that most of the spectral lines are characteristic of the **individual elements,** and not of compounds that may be formed by the union of one element with another. This is commonly explained by assuming that each kind of atom—an atom of sodium, for example—contains a definite number of electrons (§ 125) vibrating in a definite way with a definite frequency, which is unaltered by the presence of other kinds of atoms in its immediate neighborhood.

The number and intensity of the spectral lines obtained for any given element depend on the way in which the lines are induced (flame, arc, vacuum discharge). Accurate catalogues have been made which give the wave-length corresponding to each separate line in the spectrum of each element. Thousands of lines are listed, but every new one becomes the center of intense interest, for it may indicate a new element. The spectroscope was the direct means of discovering helium, rubidium, cesium, thallium, indium, gallium, and other elements.

EXERCISES

1. Give an ionic formulation of the electrolytic dissociation of fused NaOH; and electronic formulations (§ 426) of the reactions taking place at the electrodes on passing a current.

2. What quantity of sodium is produced in 10 hours by a cell carrying 50 amperes of current, assuming equal numbers of gram-ions of H^+ and Na^+ to be discharged at the cathode?

3. What volume of hydrogen gas, at standard conditions, is liberated in the preceding problem?

4. Tell how oxygen gas may be prepared from sodium peroxide. Write and balance equation.

5. What volume of oxygen gas, at 20° C. and 740 mm. pressure, is required to convert 100 g. of metallic sodium into sodium peroxide?

6. What weight of slaked lime, 95 per cent pure, is needed to causticize a ton of anhydrous sodium carbonate?

7. What volume of sodium hydroxide solution, of sp. gr. 1.18, containing 16 per cent NaOH, can be prepared from a kilogram of pure Na_2CO_3?

8. Give equations for the conversion of NaCl into Na_2S in several successive steps. State the conditions under which these reactions take place.

9. Explain why it is impossible to convert NaCl directly into Na_2CO_3 by boiling calcium carbonate with brine.

10. Na_2SO_4 may be produced by passing a mixture of water vapor, SO_2,. and air through a heated porous mass of common salt (*Hargreaves process*) Explain (*a*) why the reaction is very slow, and (*b*) why it ultimately becomes complete.

11. Write an equation to show the use of NaOH in the manufacture of soap. What is the difference in the chemical composition of hard and soft soaps?

12. How is soda-lime prepared?

13. Give equations to show what products are formed when carbon dioxide is absorbed by soda lime.

14. Give a complete *ionic* formulation of the production of sodium bicarbonate in the Solvay process.

15. How is water glass solution made, and for what is it used?

16. (*a*) Describe a method, in several steps, for converting sodium sulfate into sodium chloride. Write equations. (*b*) Why cannot this transformation be effected simply by evaporating a sodium sulfate solution with an excess of hydrochloric acid?

CHAPTER XXXIV

THE ALKALINE EARTH METALS

Sir Humphry Davy, who was the first to prepare metallic sodium and potassium (§ 430), had the honor of discovering seven of the eighty-seven elements known to us to-day—a greater number than yielded to the skill of any other investigator.* Sufficient testimony to his industry and genius is found in the fact that in 1808—just a few months after his preparation of metallic sodium and potassium—he was able to announce to the world the discovery of five additional new elements: magnesium, calcium, strontium, barium, and boron. The first four of these belong to what is now called the alkaline earth group of metals (Group II A of the periodic table) and were prepared in part by electrolytic methods quite similar to those employed in his previous investigations.

446. Chemical Characteristics of the Alkaline Earth Metals.—The alkaline earth group contains six elements: Beryllium, Be; magnesium, Mg; calcium, Ca; strontium, Sr; barium, Ba; and radium, Ra. **All of these have a valence of two in all their important compounds.** In other respects, however, beryllium is related rather to aluminum, the second element of the next following Group (III A).† Magnesium, too, is related in its chemical behavior to zinc, in Group II B.

The alkaline earth elements are all silvery bright metals, with about the general toughness and malleability of lead. All of them but barium are lighter than aluminum, and all of them melt between 600° C. (Mg) and 1000° C. (Be); in other words they melt at temperatures above the melting points of tin and lead, but below the melting point of copper.

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* Berzelius, the great Swedish chemist of a century ago (1779–1848) had the discovery of five elements to his credit: Ce, Th, Zr, Se, Si.

† This reminds one of the resemblance (§ 584) of lithium, the first element in Group I A, to magnesium, the second element of the next following Group II A; and that (§ 411) of boron, the first element in Group III A, to silicon, the second element in Group IV A.

MAGNESIUM

447. Magnesium Minerals.—1. Nearly all the silicate rocks of the earth's crust contain notable quantities of magnesium. Some of these are of commercial importance; examples are talc, soapstone, and asbestos (§ 402), which are metasilicates (§ 398); and serpentine, which is more highly silicious (a disilicate).

2. By weathering, the silicate rocks yield up their soluble constituents, and thus the ocean has come to contain enormous quantities of dissolved magnesium salts. Indeed, about 15 per cent of all the dissolved solid matter in the sea consists of magnesium chloride and magnesium sulfate—enough to cover all the land areas of the earth to a depth of 60 or 70 ft. The mother liquors from the crystallization of common salt from sea water or from the brine of salt wells are always rich both in magnesium salts and bromides. The great deposits of potassium salts in southern Germany and in France are always associated with magnesium salts, or with salts containing both potassium and magnesium (**carnallite,** § 442).

3. Magnesium carbonate, or **magnesite,** is usually found in association with calcium carbonate. In one and the same deposit, the material may vary from almost pure magnesite, $MgCO_3$, to almost pure calcite, $CaCO_3$. When the two constituents are present in roughly equi-molecular proportions, the mixture may be altered by pressure to a distinct mineral, **dolomite,** $MgCO_3 \cdot CaCO_3$. This may be associated with an excess of calcite, giving what is called **dolomitic limestone.** Dolomite is an exceedingly plentiful mineral, occurring in enormous deposits in all parts of the earth. Whole mountain ranges consist largely of this one substance.

448. Metallic Magnesium.—*Preparation.* Metallic magnesium is now prepared on a large scale from magnesium chloride, $MgCl_2$, previously dehydrated in a current of HCl gas. The anhydrous salt melts readily, furnishing a conducting liquid, which is electrolyzed in closed furnaces, in a current of coal gas, to exclude air. Magnesium has also been obtained by reducing magnesium chloride with metallic sodium.

Properties. Metallic magnesium is a silvery bright metal, somewhat resembling zinc in superficial appearance. Like zinc, too, it is malleable when heated, and may be pressed into wire or rolled into sheets. It tarnishes readily in moist air, becoming covered with a layer of carbonate. Ignited in the air, it burns with a brilliant white light, forming a mixture of the oxide and nitride, MgO and Mg_3N_2. Its tendency to unite with oxygen is so pronounced that it will even burn in a current of steam, and if heated in carbon dioxide will reduce the latter to monoxide.

Uses. 1. The light from burning magnesium happens to be unusually actinic (i.e., rich in the bluish and ultra-violet rays that affect most intensely a photographic plate). Magnesium powder, mixed with potassium chlorate or some similar oxidizing agent, is therefore used as a flashlight mixture. **(A very dangerous mixture** when carelessly handled (§ 206).)

2. *Magnalium* and *Dow Alloy* (§ 477).

3. Magnesium is now used as a deoxidizer, in the preparation of nickel alloys (§ 525).

449. Magnesium Oxide and Hydroxide.—Magnesium oxide, MgO, is commonly called **magnesia.** It is prepared by gently heating magnesium carbonate, to expel carbon dioxide.

Uses. 1. The white powder, obtained as just described, is very light and flocculent, but shrinks on being heated to a high temperature, and when sintered in an electric furnace becomes very dense and hard. This "shrunk magnesia," with a suitable binder, such as a small proportion of clay, is molded into **magnesia brick,** for furnace linings.

2. Magnesium oxide, moistened with a saturated solution of magnesium chloride, soon sets to a solid mass of **basic magnesium chloride** (assumed to be Mg(OH)Cl). This has been put to much the same uses as plaster of Paris (§ 453). It is now an important building material (flooring partitions, and "stucco").

3. Magnesium oxide unites with water to form magnesium hydroxide, $Mg(OH)_2$, the action proceeding most rapidly with the flocculent form of the material. Magnesium hydroxide is very insoluble, and less actively basic than the other hydroxides of the alkaline earth group. It is therefore useful in **pharmaceutical preparations** (mouth washes and infant foods) in which acidity is to be combated without running the risk of using an excess of alkali as would be the case if such a soluble and active substance as sodium hydroxide were employed.

(4) The flocculent form of magnesium oxide is an important rubber filler (§ 353).

450. Hydrolysis of Magnesium Salts.—When magnesium salts react with soluble alkali carbonates, a precipitate is thrown down that proves to be a **hydrated basic carbonate,** of variable composition, approximating $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O$. This is **magnesia alba,** employed as a cosmetic.

Calcium, strontium, and barium salts are precipitated by Na_2CO_3 as normal carbonates ($CaCO_3$). The fact that magnesium salts, under the same conditions, give a basic carbonate, by partial hydrolysis of the normal salt, shows that **$Mg(OH)_2$ is a less active base than the other hydroxides of the alkaline earth group.** A further proof is found in the fact that solutions of magnesium chloride on being heated are partially hydrolyzed:

$$MgCl_2 + HOH \rightleftarrows MgO + 2HCl.$$

If such a solution is evaporated to dryness and strongly ignited, the acid will at length be completely expelled and the salt all converted into magnesium oxide.

Order of Increasing Activity.

$$Mg(OH)_2,\ Ca(OH)_2,\ Sr(OH)_2,\ Ba(OH)_2.$$

Order of Increasing Resistance to Hydrolysis.

$$\overset{\xrightarrow{\hspace{5cm}}}{MgCl_2,\ CaCl_2,\ SrCl_2,\ BaCl_2.}$$

We shall presently see that many heavy metals (zinc, lead, copper, nickel, iron) resemble magnesium in their inclination to give basic carbonates, rather than normal carbonates, when precipitated with sodium carbonate, and thus betray the slight activity of the corresponding bases; while with mercury the hydrolysis is complete, and the precipitate thrown down by Na_2CO_3 is simply the oxide HgO, (§ 564).

451. "85 Per Cent-Magnesia."—A basic magnesium carbonate, of the formula $MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, has been prepared. This substance is a white powder, remarkable for its light and fluffy condition. A given volume is actually about 90 per cent pores, and only about 10 per cent solid. Mixed with asbestos fiber it makes an ideal covering for steam-pipes and boilers, and is put on the market in molded shapes, under the trade-name "85 per cent-magnesia." The money thus saved in the cost of fuel, where steam is to be transported long distances, runs into immense sums each year.

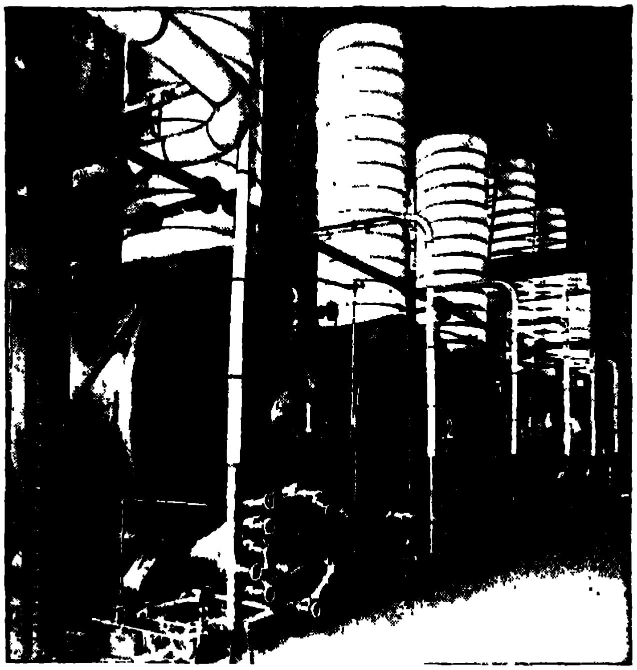

FIG 102.—A set of fractionating columns, on a row of alcohol stills, jacketed with "85-per cent magnesia," to keep the temperature uniform.

452. Analytical Tests for Magnesium.—1. Magnesium salts differ from those of the following members of the alkaline earth group in giving no lines in the visible spectrum, at the temperature of the Bunsen burner—though the camera shows several lines in the ultra-violet region (§ 445).

2. Sodium hydroxide and sodium carbonate, when added to solutions of magnesium salts, precipitate magnesium hydroxide and basic magnesium carbonate (§ 450), respectively. But if ammonium hydroxide or ammonium carbonate is used, precipitation fails to take place, or remains incomplete. This is because **magnesium hydroxide and basic carbonates are readily dissolved by solutions of ammonium salts.**

The explanation for this fact, in terms of the ionic theory, may be formulated:

$$\begin{array}{rcl}
\underset{\text{Solid}}{\mathrm{Mg(OH)_2}} \underset{(2)}{\overset{(1)}{\rightleftarrows}} \underset{\text{In solution}}{\mathrm{Mg(OH)_2}} \underset{(4)}{\overset{(3)}{\rightleftarrows}} & \mathrm{Mg^{++}}+ & \mathrm{2OH^-} \\
 & & + \\
\mathrm{2NH_4Cl} \rightleftarrows & \mathrm{2Cl^-}+ & \mathrm{2NH_4^+} \\
 & & \updownarrow (5) \\
 & & \mathrm{NH_4OH}
\end{array}$$

We think of the dissolved $Mg(OH)_2$ as partially ionizing in solution (reaction 3) to form Mg^{++} and OH^- ions. But the OH^- ions are immediately withdrawn by combination with NH_4^+ ions, to form molecules of the slightly dissociated base, NH_4OH (reaction 5). This disturbs the equilibria (1, 2) and (3, 4). The OH^- ions withdrawn are at once replaced by the dissociation of new $Mg(OH)_2$ molecules (reaction 3); and these latter are in their turn replaced from the supply of solid $Mg(OH)_2$ (reaction 1). Eventually, all of the precipitate is thus dissolved.

(3) Magnesium salts can be detected in solution only after removal of the heavy metals and the other alkaline earth metals by precipitation with NH_4OH and $(NH_4)_2CO_3$. Addition of a soluble phosphate, in the presence of ammonium hydroxide, then throws down a white, crystalline precipitate of *magnesium ammonium phosphate*, $MgNH_4PO_4 \cdot 6H_2O$:

$$MgCl_2 + Na_2HPO_4 + NH_4OH = MgNH_4PO_4 \downarrow + 2NaCl + H_2O.$$

When this salt is ignited it forms *magnesium pyrophosphate*, $Mg_2P_2O_7$.

CALCIUM

453. Calcium Minerals.—Calcium, like magnesium, is an important constituent of nearly all the silicate rocks, and is found in large quantities in the ocean, as chloride and sulfate. Calcium carbonate is the most important, and by far the most widely distributed compound of calcium. In a nearly pure condition, definitely crystallized, it is called **calcite,** or **Iceland spar. Marble, limestone,** and **chalk** are less pure forms; while **dolomite** (§ 447) is a distinct mineral, approximating the composition $CaCO_3 \cdot MgCO_3$.

Calcium carbonate dissolves in water in the presence of an excess of carbonic acid. Thus, subterranean waters that have accumulated carbon dioxide under pressure often hollow out great caves when they come in contact with limestone deposits. The beautiful stalactites and stalagmites that are formed in such caves owe their origin to the fact that the water which trickles through the roof of the cave parts with carbon dioxide as soon as the pressure upon it is released (§ 98). The calcium carbonate is accordingly deposited, and in the course of years may form a continuous column from roof to floor:

$$\underset{\substack{\text{Hypothetical}\\ \text{calcium acid}\\ \text{carbonate}}}{Ca(HCO_3)_2} = CaCO_3 + CO_2 \uparrow + H_2O.$$

The formation of scale in steam boilers is a related phenomenon (§ 459—item 4).

Second in importance among the minerals of calcium is **gypsum,** $CaSO_4 \cdot 2H_2O$.

When gypsum is heated it loses a part of its water of hydration (§ 79) and forms *plaster-of-Paris*, approximately $CaSO_4 \cdot \frac{1}{2}H_2O$, used for making replicas of statuary. Mixed with wood fiber it forms *stucco*. The setting of plaster-of-Paris is a process of rehydration, for when water is added the powder combines with this to form a mass of interlocking crystals of gypsum. Plaster-of-Paris that has been too strongly heated will not set readily, unless the process of rehydration is catalyzed, by alum or some similar substance. Such a mixture of " dead-burnt " gypsum, with a little alum, is *Keene's cement*, widely used for interior decorations in imitation of marble.

Other important calcium minerals are **fluorite or fluorspar,** CaF_2 (§ 209); **phosphate rock,** $Ca_3(PO_4)_2$ (§ 308); and colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$ (§ 411). These are the sources of the commercially useful compounds of fluorine, phosphorus, and boron.

454. Metallic Calcium.— Metallic calcium is prepared by electrolysis of the molten chloride. Sometimes fluorspar is added to lower the melting point. The cathode is a copper rod, just touching the surface of the electrolyte and gradually withdrawn as the operation progresses. The calcium adheres to the end of the rod and is thus slowly built up into an irregular cylinder of metal.

Metallic calcium melts at a dull red heat (800° C.). It is tough, and can be turned and polished on the lathe, but is a much more active element than magnesium, decomposing water slowly, even at room temperatures. This property of calcium has sometimes been employed to remove the last traces of water from alcohol, previously dehydrated as far as possible by quicklime.

Calcium unites directly with all the non-metals, including even nitrogen. It combines with hydrogen to form a hydride, CaH_2. This has been of some use as a source of hydrogen for portable balloon plants, since it decomposes water even more readily than calcium itself.

The only important calcium alloy is *Frary metal,* prepared by electrolyzing molten calcium and barium chloride, with a cathode of molten lead, and used as an anti-friction metal for bearings, replacing Babbitt metal (§ 322).

455. Limestone and Its Uses.—The quantities of calcium carbonate mined and used each year are enormous. In the United States, limestone quarries and lime-burning kilns are located in forty-three of the forty-eight states. The American Portland cement industry alone probably consumes more than 13 million tons of impure limestone each year. Great quantities of marble and high-grade limestone come from the quarries of Vermont and other New England States, and from the states of the Mississippi

Valley, to be used for building stone. Stone for concrete mixtures and roads calls for further large amounts. Several million tons more are used as fluxes (§ 416) in the smelting of iron, copper, zinc, and other metals, and for burning to quicklime (§ 456) for the preparation of mortar and for use in the chemical industries. Taken altogether, the United States consumes well over 20 million tons of limestone each year—about 400 lbs. for every member of the population. Only coal and iron mining and the production of foodstuffs turn over greater weights of raw material.

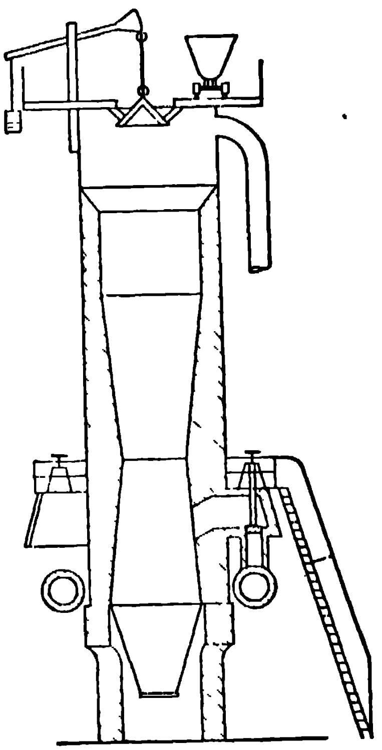

FIG. 103.—Cross-section of a stationary lime kiln, fired with producer gas.

456. Quicklime and Its Uses.—When limestone is heated to a temperature of a few hundred degrees centigrade, it is decomposed, losing carbon dioxide, and leaving behind a residue of calcium oxide (*quicklime*, or *lime*). The reaction is a reversible one, and in a closed space, at each temperature, proceeds only until sufficient carbon dioxide has accumulated to set up a definite pressure:

$$CaCO_3 + 21{,}900 \text{ cals.} \rightleftarrows CaO + CO_2.$$

Will this reaction become more or less complete from left to right as the temperature is raised? State the principle involved.

The process of decomposing limestone to produce quicklime is commonly called "limestone-burning," though "calcination" would be a better name, since the oxygen of the air is in no way connected with it. It is very often carried out in vertical furnaces (Fig. 103), fired with producer gas (§ 335); but rotary kilns (Fig. 104), similar to those employed in the manufacture of Portland cement, are now often used.

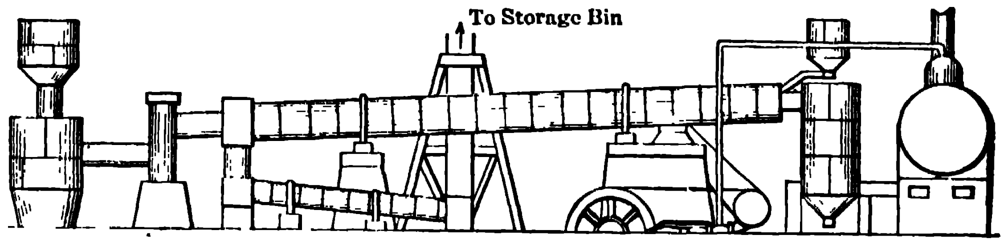

FIG. 104.—A rotary lime kiln. Compare with cement furnace, Fig. 106.

About one-third of the 3 million tons of quicklime produced in the United States each year goes into the building industry, for the production of **mortar** (plaster). This is simply calcium hydroxide (formed by slaking calcium oxide with water) mixed with a little excess of water and some sand. The setting of mortar is due in part to a slow combination of the calcium hydroxide with the carbon dioxide of the air, to form calcium carbonate. If air is excluded the process becomes impossible, and mortar (unlike Portland cement) accordingly fails to set under water. **Even in the absence of air, however, a paste of calcium hydroxide will acquire a certain degree of hardness, due to the formation of a colloidal gel** (§ 386). Mortar made from dolomitic limestone sets more slowly than that from pure limestone, and is somewhat deficient in mechanical strength, but works up more smoothly under the trowel.

Other Uses of Quicklime

Sprays and dips for combating fungi and insects (§ 537–1).
Calcium bisulfite for paper-making (§ 376).
Sand-lime brick (§ 485).
Flux for the production of pig-iron and other metals (§ 491).
Causticizing soda (§ 435).
Manufacture of soda by Le Blanc and Solvay processes (§ 435).
Removing hair from hides in tanning.
Manufacture and refining of cane and beet sugar (§ 367).
Purification of coal gas (§ 347).
Manufacture of calcium carbide (§ 457).
Manufacture of glass (§ 406).
Purification of water (§ 461).
Manufacture of bleaching powder (§ 201).
Recovering ammonia from coal gas (§ 283).
Recovery of acetic acid and acetone from the liquid produced by destructive distillation of wood (§ 360).

457. Calcium Carbide.—Calcium carbide, CaC_2, is made by the action of an excess of carbon, in the form of coke, on quicklime, in an electric furnace, at a temperature of 2800° C.:

$$CaO+3C=CaC_2+CO.$$

Furnaces are now so designed that the product melts, and may be tapped off at the bottom in a fused condition (Fig. 105). The largest furnaces now have a capacity of 10,000 horse-power.

Two very important uses for calcium carbide have previously been mentioned—the production of *acetylene* by its reaction with water (§ 346); and of *calcium cyanamide*, as a step in the synthesis of ammonia (§ 284). Calcium carbide is an excellent reducing agent, and has been used on a small scale for the reduction of the oxides of the heavy metals. Its production has increased enormously since its first commercial utilization in 1892; at the present time probably half a million tons a year are consumed.

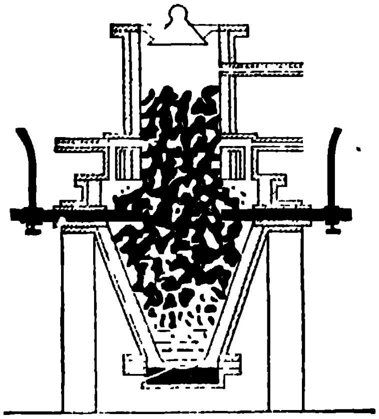

Fig 105 —A small calcium carbide furnace Large furnaces are of the design shown in Fig 98

458. Analytical Tests for Calcium.—**Calcium salts color the flame a brick-red,** and it is easy to identify the element by its characteristic **red and orange spectral bands.** Solutions of calcium salts, after the heavy metals have been removed by hydrogen sulfide and ammonium sulfide, are often precipitated as the **carbonate** (along with strontium and barium) by ammonium carbonate, from a solution made definitely alkaline with ammonium hydroxide.

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 \downarrow + 2NH_4Cl.$$

In the analysis of limestone, cement, or other substances containing calcium, the latter is usually precipitated as the **oxalate.** This, when ignited, gives the oxide, from the weight of which it is possible to calculate the percentage of calcium in the original material.

EXERCISES

1. Anhydrous carnallite has a lower melting point than pure magnesium chloride. State the principle involved. How is this an advantage in the production of metallic magnesium?
2. Calculate the percentage of MgO in pure dolomite.
3. What volume of carbon dioxide gas (§ 147) is evolved in calcining 100 lbs. of pure magnesite?
4. Why is it necessary to pass a current of coal gas through a magnesium furnace?
5. Write equations to show the action of metallic magnesium on steam and carbon dioxide.
6. Calculate the weight of powdered potassium chlorate to be mixed with 5 g. of powdered magnesium in order to get the maximum explosive effect.
7. What weight of metallic magnesium is needed to deoxidize an ingot of nickel alloy containing 250 c.c. of dissolved oxygen gas, measured dry at 20° C. and 740 mm.?

8. Give equations to explain why sea-water will corrode a steam-boiler.

9. About 167 g. of $MgCl_2 \cdot 6H_2O$ will dissolve in 100 g. of water, at room temperature. Calculate the weight of *anhydrous* salt in 100 g. of the *solution.*

10. Write and balance equations to show the result of an attempt to dehydrate magnesium nitrate, $Mg(NO_3)_2 \cdot 6H_2O$, by heating in the air. Would such a method give anhydrous barium nitrate, and why?

11. A sample of magnalium weighing 1 g. is dissolved and analyzed, producing 0.226 g. aluminum oxide, and 4.000 g. magnesium pyrophosphate $Mg_2P_2O_7$. Calculate the percentages of its principal constituents.

12. Draw up a table showing the principal uses of three calcium minerals other than $CaCO_3$, giving a chemical equation in connection with each use, where possible.

13. What volume of CO_2 gas at standard conditions (§ 147) is liberated by the decomposition of sufficient limestone to produce 1 ton of quicklime?

14. The reaction for the production of calcium carbide in an electric furnace calls for what minimum weight of anthracite coal, containing 80 per cent non-volatile carbon, for each ton of carbide produced?

15. Tabulate the principal uses of quicklime, giving one or more equations in connection with each, where possible.

16. Write an introduction to a popular article on the limestone industries, intended to show the great diversity of interests which center in this raw material.

17. Give equations to explain the nature of the difficulty met in attempting to produce anhydrous calcium chloride by ignition in the air. Tell why ignition in a current of HCl is successful.

18. A sample of impure limestone weighing 1 g. yields sufficient calcium oxalate to produce 0.520 g. of pure CaO. Calculate the percentage of $CaCO_3$ in the original sample.

CHAPTER XXXV

THE ALKALINE EARTH METALS (CONTINUED)

THE CHEMISTRY OF WATER SOFTENING

459. Calcium and Magnesium Salts in Water.—Water for domestic use must be free from objectionable color, taste, odor, and bacteriological contamination. Small amounts of suspended matter or dissolved salts are usually not considered harmful. The clarification and subsequent treatment of domestic water supplies containing more than the permissible amounts of such impurities has already been described (§ 82).

On the other hand, water for laundering, for the manufacture of paper, or for use in boilers, must be comparatively free, not only from suspended impurities, but also from dissolved salts of iron, manganese, magnesium and calcium. There are a number of reasons why these mineral impurities render water unfit for industrial use:

(1) **Iron and manganese salts** are objectionable in that they tend to be oxidized and hydrolyzed, depositing reddish flocks of ferric oxide (Fe_2O_3) or of hydrated manganese dioxide ($MnO(OH)_2$) which produce rusty spots on clothing or paper.

(2) **Magnesium salts** are hydrolyzed very readily when solutions containing them are heated (§ 450), liberating acid, which rapidly corrodes the pumps and boilers.

(3) Both **calcium and magnesium salts** react with soap solutions, throwing down a slimy precipitate—an insoluble calcium or magnesium soap:

$$\underset{\text{Sodium soap (§ 367)}}{2C_{17}H_{35}COONa} + MgCl_2 = \underset{\text{Magnesium soap}}{(C_{17}H_{35}COO)_2Mg} \downarrow + 2NaCl.$$

The precipitation not only stains fabrics washed with soap in such water, but very greatly increases the amount of soap that it is necessary to use. Water that requires a great deal of soap, in order to free it from dissolved calcium and magnesium salts, is said to be very **hard;** and the quantity of soap consumed is a direct measure of its hardness. ***Temporary hardness*, so called because it may be removed by boiling, is due to acid carbonates; *permanent hardness* is due to other salts of calcium and magnesium.**

The removal of temporary hardness by boiling, is, in principle (§ 453):

$$Ca(HCO_3)_2 = CaCO_3 \downarrow + H_2O + CO_2 \uparrow .$$

(4) On heating water having a considerable amount of temporary hardness, the $CaCO_3$ that is deposited may form a coating or **scale,** that clings tightly to the boiler tubes and interferes with the transmission of heat. A layer one-sixteenth of an inch in thickness may actually lower the efficiency of steam raising by 20 per cent, causing a fifth of all the heat generated under the boiler to be deflected up the chimney.

460. Water-softening by Precipitation.—The treatment to be given any given sample of water, in order to fit it for industrial use, will, of course, depend on the kind of impurities to be removed, and should be based upon a careful chemical analysis. If corrosion is noticed, due to the liberation of acids through hydrolysis of magnesium salts, it may sometimes be prevented by the use of scrap zinc. This metal stands higher than iron in the electrolytic series, and accordingly becomes anode when in contact with iron (§ 422) being itself dissolved by the acids present, and acting vicariously to spare the boiler itself.

If trouble is caused by the formation of scale, it may sometimes be cured by the addition of a precipitating agent, together with a little starch or tannin, or some similar organic substance, which tends to coat over the precipitated particles, to prevent them from adhering to the boiler tubes. For the most efficient purification, a scale-forming water should be treated with the precipitating agent, then run off into settling tanks or filtered.

The common precipitating agents are lime-water (calcium hydroxide solution) and soda ash (commercial sodium carbonate). **The lime-water must be added in just sufficient amount to accomplish two results. (1) To neutralize all the free carbonic acid and** other acids in the water and change the acid carbonates of calcium and magnesium to the insoluble normal carbonates:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 \downarrow + 2H_2O.$$

(2) To precipitate all the aluminum, iron and magnesium as hydroxides, leaving an equivalent quantity of calcium salts in solution:

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 \downarrow + CaCl_2.$$

Soda ash is then added in sufficient quantity to precipitate all the calcium originally present as sulfate and chloride, or formed from the added lime water:

$$CaSO_4 + Na_2CO_3 = CaCO_3 \downarrow + Na_2SO_4.$$

Water which has been correctly treated in this way, and then settled or filtered, will never form scale. But it will be noticed that in the removal of permanent hardness sodium salts are introduced. These increase the tendency of the liquid to *foam* during boiling; and in extreme cases water may be thrown out of the boiler into the steam pipes, perhaps wrecking the engine.

461. The Arithmetic of Water Softening.—Review § 118. As an example of the application of the two simple principles just discussed, let us formulate a prescription for the softening of a water of the following composition:

	Milligrams per Liter (= *Parts per Million*).	*Milligram-Equivalents per Liter.*
Suspended matter	30	....
Free CO_2	10	(0.45)
Cations		
Calcium (Ca^{++})	11.00	0.55
Magnesium (Mg^{++})	2.80	0.23
Sodium (Na^{+})	4.60	0.20
Potassium (K^{+})	1.10	0.03
	Total Cations	1.01
Anions		
Carbonate (CO_3^{--})	0.00	0.00
Bicarbonate (HCO_3^{-})	41.00	0.67
Sulfate (SO_4^{--})	6.80	0.14
Chloride (Cl^{-})	7.00	0.20
Nitrate (NO_3^{-})	0.00	0.00
	Total Anions	1.01

The first column of figures gives the results of the chemical analysis of the water expressed in *milligrams per liter*. To put these data into usable form, each number must be divided by the weight of a milligram-equivalent of the ion concerned. This gives the results in the second column of figures, in which the composition of the water is expressed in *milligram-equivalents per liter*.

Now, there must be added enough $Ca(OH)_2$ to unite with all the CO_2 (0.45 mg.-equiv.) and HCO_3^- (0.67 mg.-equiv.) in addition to precipitating all the magnesium (0.23 mg.-equiv.). This makes a total of 1.35 mg.-equivs. of $Ca(OH)_2$. Since 1 milligram-equivalent is $\frac{1}{2}(40+2\times17)=37$ mg., this will mean $1.35\times37=50$ mg. of $Ca(OH)_2$ for each liter of water treated.

We now need to add enough soda ash to precipitate all the calcium sulfate or chloride originally present in the solution, or formed just now during the precipitation of the magnesium salts with lime-water. This is most easily found by noting the total amount of sulfate (0.14 mg.-equiv.) and of chloride (0.20 mg.-equiv.) and diminishing this by the amount of sodium (0.20 mg.-equiv.) and potassium (0.03 mg.-equiv.). This gives 0.11 mg.-equiv. of sulfate and chloride, originally present in combination with calcium and magnesium, and now with calcium alone. Thus, we must add 0.11 mg.-equiv. of Na_2CO_3; or $0.11\times\frac{106}{2}=5.8$ mg. of that substance for each liter of water treated.

But a milligram in a liter is the same as $\frac{1}{120}$ lb. in 1000 U. S. gals.* Hence, each thousand gallons of water treated will require $50\times\frac{1}{120}=0.42$ lb. $Ca(OH)_2$; and $5.8\times\frac{1}{120}=0.048$ lb. Na_2CO_3. Allowing something for impurities in these chemicals, our final prescription would therefore call for about 0.45 lb. commercial slaked lime and 0.05 lb. of soda ash.

The preceding calculation is intended to illustrate the general procedure followed in calculating formulas for water softeners, but one should not attempt to follow it blindly, disregarding all other considerations. Where temporary hardness (due to acid carbonates) is high, it may be best to remove the dissolved CO_2 by heating, and then soften by the use of Na_2CO_3 alone. Again, it is sometimes necessary to be content with partial precipitation of the calcium and magnesium, in order to avoid risk of foaming, caused by the addition of too much sodium. Finally, there are cases of waters high in sulfate, which can best be softened by barium carbonate, provided they are not to be put to uses in which the poisonous nature of barium salts would be an objection.

462. Water Softening by the Permutite Process.—At the present time, a great deal of water is softened for industrial use by being passed through beds of artificially prepared silicates, resembling in composition the natural minerals called zeolites (§ 403). This material was originally called **permutite,** a modification being known as borromite. If we represent the permutite silicate by $Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot 6H_2O$ or $Na_2(Al_2Si_2O_8)$, the softening of water filtered through such material would be represented by the equation

$$Na_2(Al_2Si_2O_8)+MgCl_2 \rightleftarrows Mg(Al_2Si_2O_8)+2NaCl.$$

It is evident that the reaction consists in the replacement of the sodium of the zeolite by magnesium or calcium. When the bed of permutite has become exhausted, it may be regenerated by passing a sodium chloride solution through it; for the preceding reaction is a reversible one.

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* Or, $\frac{1}{100}$ lb. in 1000 Imperial gallons.

PORTLAND CEMENT

463. Hydraulic Mortar or Cement.—It has long been known that **by calcining limestone containing a certain proportion of clay, it is possible to produce a hydraulic mortar, differing from ordinary mortar in its capacity for setting under water, or in the absence of carbon dioxide.** The ancient Romans took advantage of this fact in preparing the cement with which they set the stones in some of their famous aqueducts and public buildings—selecting their raw materials with a skill that cannot fail to win our admiration, when we consider that they were without any of the resources of modern analytical chemistry.

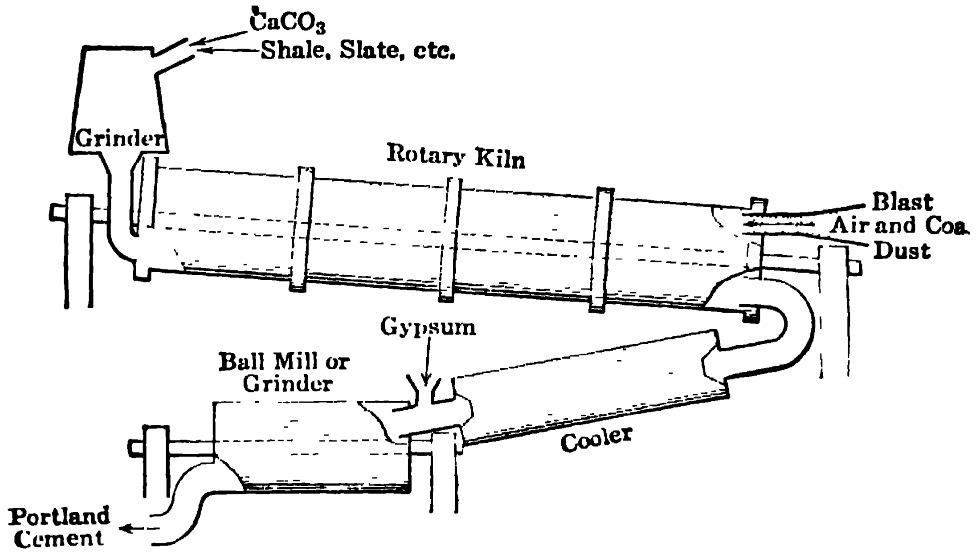

FIG. 106.—Outline of the manufacture of Portland cement.

The chemical counterpart of the ancient Roman mortar is **Portland cement,** so called from its resemblance in color to the celebrated building stone quarried near Portland, England. Invented a century ago (1824), it remained for a long time of very slight importance; but about 1890 its production began to increase by leaps and bounds, owing largely to the introduction of the rotating furnace and the invention of reinforced concrete—a device whereby the remarkable resistance of concrete to disruption by crushing is supplemented by the enormous tensile strength of steel. Fortunately, these developments found a plentiful supply of cheap reinforcing material at hand, as a result of the newly perfected Bessemer process for making steel (§ 496).

464. Concrete.—Cement mixed with sand and broken stone forms concrete, our most important building material. Cheap, strong, made of raw materials to be found in limitless quantities in every land, concrete has rapidly displaced other building materials in many an application. Wood is subject to destruction by insects, fire, and mold; stone needs to be laboriously shaped by hand; bricks have to be set in mortar, one by one, by skilled workmen. But concrete is mixed by automatic machinery, and poured into place in the rising walls like so much water, to harden in a few days to solid rock—non-inflammable, non-rusting, proof against decay, strong enough to weather earthquakes and hurricanes, and fit to endure for centuries.

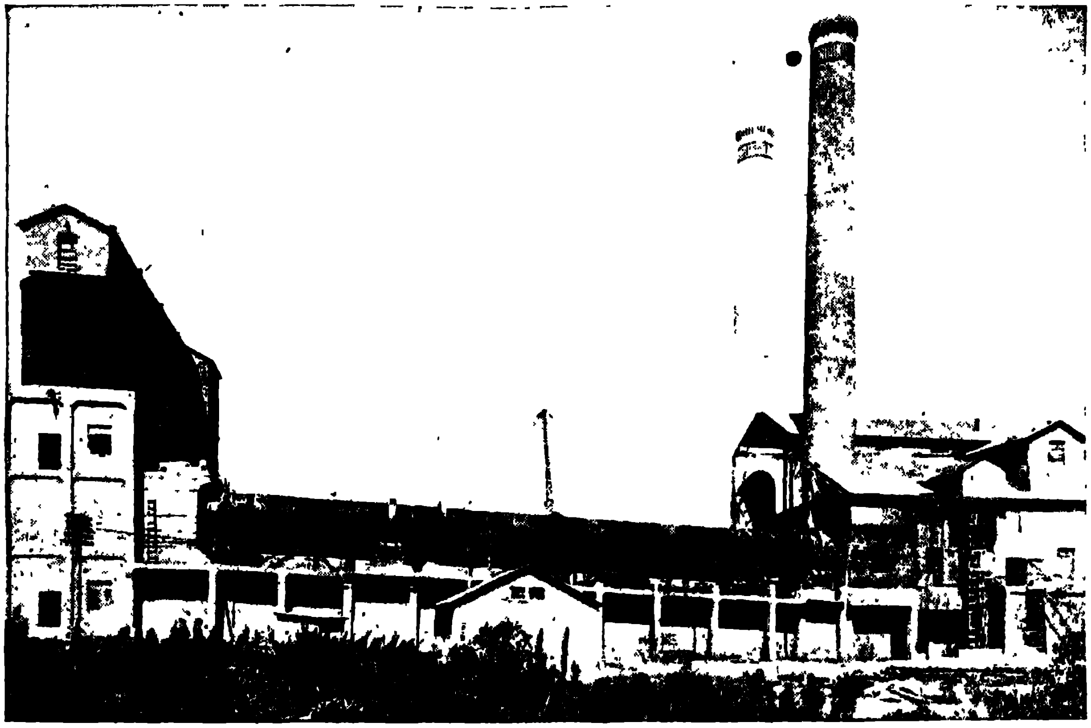

FIG. 107.—A rotary cement kiln.

Cement factories are now found in more than half the states of the Union, and most of our important engineering structures, built within the past twenty years, are of concrete: the locks of the Panama canal; the great irrigation dams in Arizona, Nevada, and Wyoming; the breakwater at Galveston; the Chicago municipal dock; aqueducts for the cities of New York and Los Angeles; several thousand miles of concrete roadbed in the states of the Ohio valley; great buildings in half a hundred cities; warehouses and grain elevators through all the Central Northwest—without counting many minor applications, such as fence-posts, fireproof shingles, culverts, tunnels, bridges, barges, and piles for restraining the Missouri River and its tributaries from encroaching on Western farms. The United States now consumes above 90 million barrels (17 million tons) of Portland cement each year.

465. Portland Cement Manufacture.—We have now long since passed the stage of being dependent on the supplies of limestone that chance to contain just the proportion of clay to give a mortar setting under water. Modern cement is produced by deliberate mingling of raw material rich in **lime** (CaO) with other material rich in **alumina** (Al_2O_3) and **silica** (SiO_2). The lime is commonly furnished by limestone of a rather inferior grade, carrying a few per cent of impurities; or in some cases by chalk or marl (a deposit of mixed chalk and clay dredged from ponds or river bottoms). The alumina (Al_2O_3) and silica (SiO_2) are furnished by clay, shale, slate-rock, or occasionally by blast-furnace slag.

The manufacture of Portland cement is carried out in four stages, as outlined in Fig. 106:

(1) **The dry materials are finely ground and mixed, in the proportion of about 4 or 5 parts of limestone to 1 of shale or clay.** The mixing must be very intimate, and in the " wet process " is aided by the addition of enough water to the finely ground material to form a thin paste of " slurry."

(2) **The wet " slurry "** (**or the intimate mixture of powdered dry limestone and clay**) **is fed into a cement furnace** (Fig. 107)—a revolving inclined tube from 6 to 8 ft. in diameter, and 60 to 150 ft. long, of sheet steel, lined with fire-brick.

The furnace is fired at the lower end, through a stationary hood of fire-brick, with a blast of compressed air and powdered coal. This end is at an intense white heat, about 1400° to 1600° C. As the flames sweep through the furnace they are cooled by the material that is being dried and calcined, and escape at the upper end at a temperature of 600° or 800° C. into a chamber lined with fire-brick and surmounted by a steel stack. In some plants, a considerable part of the power that is required for grinding and other operations is obtained from steam boilers making use of waste heat from the furnace gases.

The raw material, in passing through the furnace, is dried and calcined, CO_2 being expelled from the limestone, leaving CaO. This unites chemically to some extent with the alumina and silica to form silicates and aluminates, the excess lime being held in solid solution. The product is then discharged in the form of pellets or balls of a greenish-gray color, partially fused on the surface. A large furnace may produce as much as a thousand barrels (200 tons) of this " cement clinker " in a single day.

(3) **The clinker is cooled by passing through a cooler, a rotating cylinder, traversed by a current of cold air. It is there mixed**

with about 2 or 3 per cent of gypsum (§ 453), which has the effect of lengthening the time required for the cement to set.

(4) **The mixture of clinker and gypsum is finally ground to an extremely fine powder in rotating tubes partially filled with steel balls.**

466. Chemical Composition of Portland Cement.—Portland cement varies somewhat in chemical composition, and accordingly has no definite formula. To be of good quality it must satisfy the following requirements:

(1) **The proportion of alkalies, Na_2O and K_2O, must be very small,** and it must not have more than 5 per cent MgO or 3 per cent SO_3. Clinker containing too much of any of these constituents will fuse too readily in the furnace, and will give a cement of inferior strength.

(2) **The ratio of lime and magnesia ($CaO+MgO$) to the other principal oxides in the cement ($SiO_2+Al_2O_3$) should lie between 1.8 and 2.1.** This means that Portland cement is distinctly basic in its chemical nature—being in that respect in sharp contrast to glass, which may contain the same oxides, but with SiO_2 in considerable excess. If too much CaO is present, the cement will crack in setting and be of poor mechanical strength. If too little CaO, the cement will set too quickly.

(3) **The ratio of SiO_2 to Al_2O_3 should be 2.5 to 4.0.** The lower figure tends to give too quick a rate of setting; but in case of need the setting may be retarded by the addition of a little extra gypsum.

A cement satisfying the preceding requirements would have a composition not far from the following. CaO, 64 per cent; SiO_2, 22 per cent; Al_2O_3, 7 per cent; FeO, 4 per cent; SO_3, 1.6 per cent; MgO, 0.8 per cent; Na_2O and K_2O, 0.6 per cent. The essential constituents are, of course, the first three listed. A cement devoid of iron and manganese would be pure white, but would offer no other advantage.

467. How Portland Cement Sets.—When cement is mixed with water alone or with water plus sand and gravel, it takes an **initial set** within a few hours and thereafter hardens slowly through a period of months or years. The final strength of the concrete depends largely on the ratio of water to cement in the original mixture. Microscopical examination shows that each of the original particles of clinker has partly dissolved in water and that this dissolved material has then been redeposited around a nucleus of unchanged clinker, forming a mass of interlocking crystals. Concerning the exact chemical nature of this crystalline material there has been considerable debate; but it seems likely that the initial set is due to the formation of **crystals of a calcium silicate and calcium aluminate** of variable composition, containing a rather strong preponderance of base. Thereafter, during the final stages of hardening, **crystals of calcium hydroxide** may appear; though **the setting is partly, at least, a colloidal phenomenon,** as in the hardening of mortar (§ 456).

The fact that Portland cement sets in this way proves it to be not entirely insoluble in water, and concrete structures are consequently not altogether proof against injury if water is permitted to percolate through them. Some degree of protection is afforded by adding a small amount of lime plus gypsum to the cement in the outer layers of the concrete, or by painting the finished surface with asphalt paint. Sea water is especially destructive, for the magnesium salts rapidly dissolve out the excess of lime contained in the concrete, and structures not well protected against such corrosion are certain to be destroyed within a few years.

STRONTIUM AND BARIUM

468. Strontium.—The common strontium minerals are the **carbonate** and **sulfate,** both extremely insoluble in water. The soluble salts of strontium, such as the nitrate and chloride, are usually prepared by dissolving the carbonate in the corresponding acid; or else by reducing the sulfate with carbon at a white-heat, and then treating the product with an acid:

$$SrSO_4+4C=SrS+4CO\uparrow.$$

$$SrS+2HCl=SrCl_2+H_2S\uparrow.$$

Occasionally the sulfate is converted into the carbonate directly, by boiling with an excess of sodium carbonate solution (§ 418).

Strontium hydroxide forms a slightly soluble, crystalline, " addition compound " with sucrose, and has therefore been used in recovering sugar from molasses. Strontium salts are used in pyrotechnics, the common red fire used in signaling being a mixture of strontium nitrate with about one-fourth its weight each of $KClO_3$, S, Mg, C. (Ground separately. **Very dangerous,** § 206.) The spectrum of strontium shows a series of red bands and a single characteristic blue line.

469. Barium.—Barium likewise occurs as the insoluble carbonate (witherite) and sulfate (heavy-spar), which are converted into soluble barium salts by the methods just described for the corresponding strontium compounds. **All barium salts are extremely poisonous.** The nitrate is used as "green fire" in pyrotechnics, and the sulfate, in a very finely divided condition, is an important filler, or extender (§ 554), in the manufacture of white paints. The barium spectrum shows a number of red, orange, yellow, and green bands. Barium peroxide, BaO_2, made by heating barium oxide to about 500° C., is of some importance in the preparation of hydrogen peroxide, and was formerly used in the commercial preparation of oxygen (since it loses oxygen at high temperatures, and then recombines with a further quantity when the temperature is lowered).

EXERCISES

A. (459–462). 1. In the clarification of water by the use of alum and lime (§ 82) what weight of pure slaked lime is necessary for the precipitation of 1 lb. of crystallized alum? (§ 479.)

2. What weight of soap (assumed to be 80 per cent sodium stearate, $C_{17}H_{35}\cdot COONa$, and 20 per cent water) will be precipitated by 1000 gal. of water containing 100 mg. Ca^{++} and 100 mg. Mg^{++} per liter.

3. A water having about equal quantities of temporary and permanent hardness, is put through a feed-water heater, then filtered previous to admission to the boiler. What will be the effect on the quantity of the scale formed?

4. What relationship exists between total cations and total anions in a water, expressed in mg.-equivs. per liter (table, § 461). Explain.

B(463–469). 5. What weight of clay containing 30 per cent CaO, will need to be mixed with limestone, containing 53 per cent CaO, in order to produce a ton of unburned cement mixture, containing 42 per cent CaO? Will the cement clinker produced contain a higher or lower per cent of lime than this, and why?

6. Give equations for the following:
   Preparation of strontium acetate from strontium sulfate (2 ways).
   Preparation of strontium chloride from strontium nitrate.
   Preparation of barium sulfide from heavy spar.
   Preparation of barium hydroxide from barium oxalate (2 steps).
   Preparation of barium thiosulfate, using barium carbonate, sulfur, air, and water as raw materials (several steps).

7. Does the following Portland cement have a satisfactory chemical composition, and if not in what respect is it deficient: CaO, 65 per cent; SiO_2, 20 per cent; Al_2O_3, 9 per cent; FeO, 3 per cent; MgO, 2 per cent; SO_3, 1 per cent?

CHAPTER XXXVI

ALUMINUM

The element aluminum is the basis of the oldest, as well as some of the newest of the chemical industries. In the form of clay, it furnishes raw material for the ceramic arts the manufacture of *bricks*, *tiles*, *pottery*, *chinaware*, and *porcelain*. The history of these, if it could be written, would be as old as humanity itself.

But, side by side with such uses of the compounds of aluminum, the beginnings of which are concealed in remote antiquity, we have a group of typically modern developments, perfected within the memory of the present generation: the manufacture of *metallic aluminum*, thousands of tons each year, by the reduction of purified aluminum oxide in electric furnaces harnessed to the cataracts of Niagara; the *thermite process*, by which a whole group of metals, previously unknown to industry, have been divorced from union with oxygen, and made available in elementary form: the production of *artificial emery*, on an enormous scale, by sintering aluminum oxide in an electric arc, for use as an abrasive in grinding machine parts to exact dimensions; the manufacture of aluminum nitride, with the aid of nitrogen from liquid air, as a stage in the synthesis of ammonium salts, for increasing the fertility of the soil; not to mention the *Portland cement industry*, consuming vast quantities of clay of an inferior grade, together with limestone, to produce a building material superior to any that the ancient world ever knew.

470. Aluminum Minerals.—Aluminum is found in a great many silicate rocks and minerals (feldspar, § 402; mica, § 407) and in all soils. Every clay-bank, too, is a potential aluminum mine; but, at the present time, even the purest of clay deposits cannot profitably be exploited for the production of aluminum and its salts, in competition with the more valuable aluminum minerals.

1. **Bauxite,** the chief of these, is the commercial source of metallic aluminum. It is a hydrated form of aluminum oxide, approximating the formula $Al_2O_3 \cdot 2H_2O$.

2. Another aluminum mineral—important because it is used as a solvent for bauxite in the preparation of metallic aluminum—is **cryolite,** or sodium-aluminum fluoride, Na_3AlF_6. The principal source of this is in Greenland, where great quantities are mined and exported yearly to the United States and Europe.

3. **Kaolin,** or **China clay,** is a very pure, white, non-plastic, difficultly fusible form of clay, approximating the empirical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It is used in the manufacture of porcelain, and in sizing paper (§ 371).

471. Hydrous Aluminum Oxide.—Review §§ 94, 401. When ammonium hydroxide is added to a solution of an aluminum salt, a gelatinous white precipitate (or **gel**) is obtained. This is commonly formulated as aluminum hydroxide, $Al(OH)_3$:

$$AlCl_3 + 3NH_4OH = Al(OH_3) \downarrow + 3NH_4Cl.$$

But the gel, as a matter of fact, contains a considerable amount of water over and above that indicated by the formula. For $Al(OH)_3$ is the same, in percentage composition, as $Al_2O_3 \cdot 3H_2O$; whereas the freshly precipitated material, when drained and pressed as dry as possible, is still more than half water, and corresponds roughly to the formula $Al_2O_3 \cdot 8H_2O$. When this highly hydrated gel is exposed to a dry atmosphere, it loses water by insensible gradations, passing over imperceptibly into the anhydrous condition. No halt is made either at $Al_2O_3 \cdot 3H_2O$ or at $Al_2O_3 \cdot 2H_2O$. The former substance, or its equivalent, $Al(OH)_3$, thus fails to satisfy the test for a chemical compound, that it shall have *a definite chemical composition, maintained without variation over a definite (though perhaps limited) range of temperature and pressure.*

In brief, then, **there is probably no such thing as aluminum hydroxide.** That term, or the formula, $Al(OH)_3$, is a conventional symbol for a substance of variable composition that should properly be called **hydrous aluminum oxide.** The same is true of most of the other gelatinous precipitates commonly designated as hydroxides of the heavy metals—such things as $Fe(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$.

472. Alundum.—Aluminum oxide, like magnesium oxide (§ 449) decreases greatly in volume if heated in an electric furnace. The sintered product is extremely hard, and identical in chemical composition with the natural minerals, **emery** and **corundum.** It is commonly called **alundum,** and is very much used for making abrasive wheels for grinding automobile valves and other small machine parts that require to be finished with a very high degree of precision.

Alundum is not quite so hard as carborundum (§ 414); but it is less brittle, and therefore somewhat more economical as an abrasive for materials of high tensile strength, such as steel. For those of low tensile strength, such as brass, zinc, stone, and wood, carborundum is usually preferred.

Alundum has also been used in slip-proof blocks in stairways and subway entrances. When mingled with a small proportion of clay, to serve as a binder, it has been employed in molding crucibles for melting metals, and in filtering corrosive liquids.

473. Aluminum Oxide an Amphoteric Substance.—When any one of the hydrous forms of aluminum oxide is heated, it parts with its water. The anhydrous oxide, Al_2O_3, is commonly very insoluble in dilute acids and alkalies; but if it is dehydrated slowly, in the presence of ammonium salts, it may remain readily soluble. It is **amphoteric** (§ 414); for it dissolves in acids to form aluminum salts.

$$Al_2O_3 + 6HCl \rightleftarrows 2AlCl_3 + 3H_2O;$$

and in alkalies to form aluminates,

$$Al_2O_3 + 2NaOH \rightleftarrows \underset{\text{Sodium metaluminate}}{2NaAlO_2}{}^* + H_2O.$$

An excess of sodium hydroxide over that indicated by this equation is required to bring Al_2O_3 into solution, since the reaction is reversible. The aluminates, in other words, are **strongly hydrolyzed** by water. They are, moreover, completely decomposed, even by so slightly active an acid as carbonic acid, giving a precipitate of aluminum hydroxide.

Write equation.

474. Production of Metallic Aluminum.—Over 100,000 tons of metallic aluminum **are now produced each year by the electrolysis of a solution of purified aluminum oxide in molten cryolite.** The principal raw material is bauxite, which is separated from impurities, such as ferric oxide and silica by being dissolved in sodium hydroxide solution. The solution thus obtained is precipitated with carbon dioxide, as just described.

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* The solution may also contain sodium orthoaluminate, Na_3AlO_3; but the present tendency is to explain the dissolving of Al_2O_3 in an alkaline solution as being due, in a large measure, to its colloidal nature, which makes possible its peptization (§ 390) by adsorbed alkali.

The furnace, shown diagrammatically in Fig. 108, consists of an iron box lined inside with carbon blocks, which serve as a cathode. The anode consists of a set of carbon plates, which are lowered from the ceiling by means of a block and tackle. After an arc has been struck, some cryolite is thrown in, melting readily to a clear conducting liquid. Purified anhydrous aluminum oxide is then dissolved in this. The aluminum that is produced collects at the bottom of the furnace, and is tapped out from time to time and cast into bars or ingots.

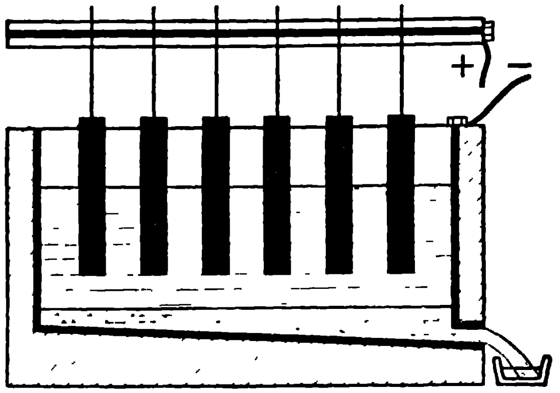

Fig. 108.—Cross-section of an aluminum furnace.

475. Mechanical Properties of Metallic Aluminum.—Metallic aluminum has great tensile strength, is extremely light, and rusts only superficially. When heated to about 100° C., it has considerable malleability, and can be shaped by stamping (milk-cans and bottles). It is easily drawn into wire if alloyed with about 1 per cent each of nickel and copper.

The colored covers on magazines are now very largely printed from aluminum plates. Aluminum foil has partly replaced tin for wrapping confectionery and tobacco. Aluminum and its lighter alloys can be cast into molds only if special precautions are observed. It may be welded with an oxy-acetylene flame, using an excess of acetylene and a flux of aluminum and lithium chlorides. Aluminum often replaces zinc in galvanizing iron (§ 503).

Aluminum has greater electrical conductivity than copper, for conductors of equal weight per lineal foot; it has been widely used in high-tension lines, where it is necessary to have the supports separated from one another by great distances.

476. Chemical Properties of Metallic Aluminum.— Although aluminum does not rust perceptibly at ordinary temperatures, large pieces, if heated to redness, will ignite and burn with a brilliant white light, to form the oxide, though not so vigorously as magnesium. Aluminum will combine directly with nitrogen, if heated in this gas, forming a **nitride,** AlN. It is therefore used for removing dissolved air from molten steel (§ 496). For years past, more aluminum has been consumed in this way than **in all** other uses combined.

Aluminum dissolves readily in dilute acids; but even concentrated nitric acid, strange to say, has very little action. Dilute alkalies attack aluminum, forming soluble aluminates, and liberating hydrogen (§ 70):

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \uparrow .$$

477. Aluminum Alloys.—The most important aluminum alloy is **magnalium,** which contains 5 to 30 per cent magnesium. It is tough and strong, and is free from a fault of pure aluminum, in that it does not adhere to lathe tools or a file. **Aluminum bronze** (90 per cent Cu, 10 per cent Al) has a beautiful golden luster, is resistant to corrosion, and is stronger than ordinary bronze (§ 531). **Nickeloy,** an alloy of aluminum with small amounts of nickel (1 per cent) and copper (4 per cent), gives castings that are free from defects, very light, and of great mechanical strength. A similar product, **Y-alloy,** (Al, 92½; Cu, 4; Ni, 2; Mg, 1½) is as light as aluminum, as tough as mild steel, very ductile, free from tendency to crack in rolling, and very resistant to corrosion.

With the proportions reversed, and nickel in large excess, we have alloys used for jewelry, possessing the beautiful luster of platinum, but without the brittleness that pure nickel shows when rolled or hammered (§ 525).

478. The Thermite Process.—When a mixture of **powdered metallic aluminum and ferric oxide** is ignited in an open crucible, a violent reaction takes place, the aluminum being oxidized by the oxygen contained in the ferric oxide:

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + 185{,}000 \text{ cal.}$$

So much heat is thus set free, and in so short a time, that the whole contents of the crucible is raised to a white heat. The iron reduced in the process is instantly melted, and collects in the bottom in the molten condition, covered over and protected from oxidation by a layer of fluid slag (Al_2O_3).

Use is now made of this reaction in *thermite welding.* The broken casting is surrounded by a mold of sand and clay, and heated to redness at the surfaces to be joined, by means of a gasoline torch. If white-hot iron is tapped into the mold, from the bottom of the reaction crucible, the heated surfaces actually melt and mingle with the added material, forming a perfect weld. Repairs have often been made by this means to ships at sea and to disabled heavy machinery of all kinds at a distance from a repair shop. A very considerable economy is effected by thermite welding of rails on electric traction systems, for the purpose of decreasing electrical resistance.

The thermite process has also been of great service in the reduction of metallic oxides, having the great advantage of producing metal free from carbon. Manganese, chromium, titanium, molybdenum, uranium, tungsten, boron, silicon, and a number of other elements have thus been prepared in a nearly pure condition or alloyed with iron. Sometimes a mixture of calcium and silicon is substituted for aluminum, in order to get a more fluid slag.

479. Aluminum Salts.—1. The most important aluminum salt, by far, is aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, which is consumed to the extent of thousands of tons each year in the purification of drinking water (§ 82), as a mordant in dyeing (§ 372), in sizing paper (§ 371), and in the tanning industry. All of these uses, except the first, depend on the fact that aluminum sulfate and **aluminum salts in general are at least partially hydrolyzed by water** (§ 414):

$$Al_2(SO_4)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H_2SO_4.$$

The aluminum hydroxide (hydrous aluminum oxide) thus formed adsorbs dyestuffs; fills the pores of paper; or interpenetrates the fibers of the hide that is being tanned, altering its texture.

2. When a solution of aluminum sulfate is mixed with one of potassium sulfate, the two salts combine to form **alum,** which is a "double salt," potassium aluminum sulfate, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, sometimes written $KAl(SO_4)_2 \cdot 12H_2O$. This is much less soluble than either of the two salts from which it is produced, and presently separates in well-formed crystals.

It is interesting to notice that ordinary alum is but one of a series of beautifully crystalline double salts, which may be formed by the union of **one gram-molecule of the sulfate of a univalent metal,** such as Li, Na, K, Rb, Cs, NH_4, Tl^{I}, with **one gram-molecule of the sulfate of a trivalent metal,** such as Al, Cr, Fe^{III}, Mn^{III}, Tl^{III}. These double sulfates are all referred to as **alums,** even though the trivalent metal contained in them is not always aluminum. Their general formula is

$$M_2^{I}SO_4 \cdot M_2^{III}(SO_4)_3 \cdot 24H_2O, \quad \text{or} \quad M^{I}M^{III}(SO_4)_2 \cdot 12H_2O,$$

and they all crystallize in very nearly identical crystal forms.

3. When metallic aluminum is heated in a current of chlorine gas or hydrochloric acid gas containing a trace of moisture, the

anhydrous salt is formed. This sublimes as a white powder, which can be collected and preserved in sealed glass tubes. **Anhydrous aluminum chloride serves as a *catalytic agent* in many important organic syntheses** (see text-tooks of *Organic Chemistry*, Friedel and Crafts' reaction).

480. Analytical Tests for Aluminum.— There are no characteristic color tests by which aluminum salts may be identified in solution.

1. **Ammonium hydroxide,** however, or a limited amount of sodium hydroxide, added to a solution of any aluminum salt, throws down a white, gelatinous precipitate of aluminum hydroxide (*i.e.*, hydrous aluminum oxide, § 471):

$$Al_2(SO_4)_3+6NH_4OH=2Al(OH)_3\downarrow+3(NH_4)_2SO_4.$$

This precipitate fails to dissolve in an excess of ammonium hydroxide (distinction from Cu, Ni, Fe'', Zn); but an excess of sodium hydroxide dissolves it (§ 473).

2. **Hydrogen sulfide,** in neutral or acid solution, produces no precipitate with aluminum salts.

3. **Alkali carbonates and sulfides** (or H_2S in an alkaline solution) precipitate aluminum hydroxide. This is because aluminum carbonate and sulfide, being salts derived from a slightly active base ($Al(OH)_3$) and slightly active acids, are completely hydrolyzed by water (§§ 113, 269).

Give molecular and ionic formulations of this hydrolysis.

4. When aluminum hydroxide, precipitated by any means, is mixed with sodium carbonate, moistened with a solution containing a mere trace of cobalt nitrate, and fused on platinum or charcoal, a characteristic blue color is produced. This is commonly assumed to be cobalt aluminate (Thénard's blue):

$$Na_2CO_3+Co(NO_3)_2=CoCO_3+2NaNO_3;$$

$$CoCO_3+2Al(OH)_3=\underset{\text{Cobalt aluminate}}{Co(AlO_2)_2}+3H_2O+CO_2.$$

The same substance is produced when cobalt oxide is used as a pigment in painting chinaware, since it reacts with the alumina of the underlying material when the piece is fired in the furnace. But an excess of cobalt oxide, in any case, gives only a black color.

EXERCISES

1. Write equations for the successive steps in purifying bauxite and preparing potash alum from the product.

2. Write equations for the production of metallic manganese and silicon by the thermite process.

3. Calcium liberates more heat per gram-equivalent than aluminum, when burned in oxygen. What does this indicate about the possibility or impossibility of producing metallic calcium from quicklime by the thermite process?

4. What are alums? Give formulas of several.

5. What is the percentage of chromium in a ferro-chrome alloy prepared by reducing pure chromite (§ 506) by the thermite process?

6. What is the chemical nature of thermite slag? For what may it be used? What other natural and artificial materials have the same composition?

7. Give an equation for the production of aluminum, electrolytically. What weight of bauxite is needed for a ton of aluminum?

8. Explain (§ 127) why aluminum bronze cannot be prepared by electrolysis of a solution containing copper sulfate and aluminum sulfate.

9. Explain why solutions of all alums have an acid reaction.

10. A sample of magnalium weighing 0.500 g was dissolved in an excess of hydrochloric acid, and an excess of ammonium hydroxide added. The precipitate formed, when collected and strongly heated, weighed 0.820 g. Calculate the percentage composition of the alloy.

11. What are some of the elements that have been prepared by the thermite reaction? What elements might be substituted for aluminum in the thermite mixture?

12. Starting with metallic aluminum, write and balance equations for reactions by which it would be possible to prepare, in succession: aluminum chloride, aluminum sulfate, alum, hydrous aluminum oxide, aluminum nitrate, sodium aluminate, aluminum acetate, aluminum phosphate.

13. Given a mixture of bauxite and carnallite, how could you prepare pure potash alum and pure epsom salts?

14. Write equations for the reactions, if any, which take place when a solution of aluminum chloride is treated with: $NaOH$, $NaOH$ (excess), Na_2CO_3, Na_2S, NH_4OH, Na_2O_2, $Ba(OH)_2$, H_2SO_4, $Na\ PO_4$.

15. Give equations for reactions by which you could distinguish between solutions of the sulfates of K, Mg, Al, Ca.

16. Give an equation to illustrate the property of aluminum acetate that makes it valuable as a mordant.

CHAPTER XXXVII

THE CERAMIC INDUSTRIES

"Let us make brick and burn them thoroughly"– Genesis 11:3.

481. Origin of Clay.– When granite and certain related rocks are exposed to weathering, they are gradually disintegrated and their more soluble ingredients dissolved and removed. In the end, all the soda and potash may disappear, leaving a residue of alumina and silica in a hydrated condition. This we call **clay.** The purest clay (kaolin) approximates the formula

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O;$$

but its composition varies somewhat with the circumstances under which it is formed. Ordinary clay is, furthermore, almost always intermingled with undecomposed fragments of the original rock, such as flakes of mica.

482. Clay for Industrial Uses.— If pure clay were known and available to the industries, it would be found to lack many useful properties that are found in impure forms of the same material. Thus, clay which is associated in nature with the proper amount of calcium carbonate may be burned directly to Portland cement (§ 465). That containing considerable fine sand may be plastic enough to mold into pottery (§ 487), yet free from the distortion by shrinkage during drying that would be shown by a purer material. That containing a small amount of ferric oxide is suitable for ornamental brick and tile, since it develops beautiful red or buff tints when baked in a kiln.

But it is often the *physical properties* of a clay, rather than its chemical composition, that determine the industrial use to which it can be put. For example, a chemical analysis reporting the presence of a definite percentage of SiO_2 would fail to reveal how much of this existed as uncombined silica, how much was present in combination with bases to form silicates, and how much in the aluminosilicic acids of the hypothetical clay substance. Again, a determination of water remaining after drying at a moderate temperature, but expelled on heating to redness, would not tell us how much of this water was held by colloidal substances, conferring *plasticity* on the clay, and how much represented replaceable hydrogen of the aluminosilicic acids, conferring *reactivity toward bases.* Finally, a difference in the percentage or state of combination of the alkali or alkaline earth metals, too small or subtle to be readily detected by analysis, may cause such a great difference in the temperature at which clay begins to fuse as to render it almost worthless technically.

483. Commercial Grades of Clay.—**Ball clay** is a relatively pure material of unusually high plasticity, which begins to vitrify (§ 485) at a fairly low temperature, and usually burns to a pure white color. These properties make it valuable for the manufacture of earthenware and stoneware (§§ 487, 488).

China clay is a variety of kaolin (§ 470) deposited in the neighborhood of igneous rocks, from which it is formed by weathering. It is used in the manufacture of chinaware, and for coating paper (§ 371). When freed from coarser material by washing with water, it is the purest known form of clay.

Fire-clay is resistant to heat, with a softening point above 1500° C. It is somewhat purer than ordinary clay, being in this respect allied to kaolin; though a chemical analysis will scarcely enable its softening point to be foretold. It has also an unusually small shrinkage when ignited, and is resistant to abrasion.

Fuller's earth is an impure type of clay, used as a filtering medium, for decolorizing edible oils.

Shale is clay which has been compacted by pressure, forming brittle, leaf-like layers of considerable hardness. We have noted (p. 309) the occurrence, in such material, of organic matter capable of yielding oil by destructive distillation. Shale is an important raw material in the Portland cement industry (§ 465).

Slate is a dense form of shale, which has been altered by heat. It is devoid of plasticity, and is used as building material, for roofing, and for electrical switchboards.

484. Classification of Ceramic Products.—Glass is a substance of acidic nature, in the sense that it contains a predominating proportion of silica (§ 406). Portland cement, on the other hand, contains an excess of base (lime). The true ceramic products—pottery, earthenware, porcelain, and the like—occupy, in a general way, a position between these two extremes; they contain less silica than glass, less lime than cement, and more alumina than either. Yet the products of the ceramic art are of the most diverse chemical composition, clay being but a minor ingredient of chinaware and porcelain; moreover, the glazes used on earthenware are of a glassy nature.

Ceramic products are conveniently classified into three groups:

1. **Unglazed porous material:** bricks, pottery, terra cotta.
2. **Porous material, glazed superficially:** earthenware, sanitary ware.
3. **Non-porous material:** stoneware, chinaware, porcelain.

We shall consider these in the next few pages.

485. Brick. – 1. Common building brick is made of loamy clay, that is, **clay containing a considerable proportion of fine sand.** The material is kneaded with water, and the dough-like mass thus produced is pressed through a rectangular opening and cut crosswise with wires. The presence of the sand lowers the plasticity of the raw material, but decreases its tendency to crack, twist, or shrink unduly during drying.

The fully dried material is heated until it begins to **vitrify.** This means that a temperature is finally reached at which **the more fusible constituents begin to melt, forming a slag which flows around the unfused particles, cementing them firmly together.** The further this process of **vitrification** is carried, the tougher, harder, and more impervious the brick will be. When it has been carried as far as is practicable without danger of causing the molded mass to lose its shape, the ceramic material is said to be **completely vitrified.**

Sometimes powdered magnesite is added, to serve as a flux, uniting with the acidic constituents of the clay to form an easily fusible alumino-silicate, thus lowering the temperature at which vitrification begins. Commonly, ferrous oxide serves as the fluxing agent, this being a more active base than ferric oxide (§ 504) and practically always present in the material being fired, through the reducing action of the flames or of organic matter present in the clay itself. The red color of the finished brick is, of course, dependent on the access of sufficient oxygen, during the later stages of burning, to oxidize the iron in the surface material to the ferric condition.

2. **The mechanical strength of brick depends on the fineness, plasticity, and moisture content of the original material, the pressure used in molding, and stage of vitrification.** Common building brick will withstand a pressure of hardly more than a thousand pounds per square inch; but thoroughly **vitrified brick,** for paving or engineering construction, will carry ten times that load.

Since brick is a cheap and heavy material, it is never transported long distances by rail, unless it happens to be of a very special quality. There are brickyards in every part of the United States though the most important production is in the Hudson River Valley, within short distances of half a dozen great cities. The total value of the brick produced in the United States (1910) amounts to more than $60,000,000 a year.

3. **Sand-lime brick** (**artificial stone**) is made by molding sand with 1 or 2 per cent of slaked lime, then treating the product for a number of hours with superheated steam. The lime reacts with a portion of the sand to form a calcium silicate, which binds the sand particles together.

486. Refractory Brick.– Many of our most important industrial products would be quite impossible to prepare without the aid of chemical substances of an extremely infusible nature, termed **refractories.** Thus, without fire-clay or a suitable substitute from which to make melting pots, we should be without glass. Lacking dolomite brick or a refractory of similar nature, we should be without basic open-hearth steel (§ 497); and the United States, which now leads the world in the production of iron and steel, would have to yield its place to countries possessed of a purer supply of iron ore.

The most widely used refractory is **fire-clay** (§ 483). Common fire-brick are molded of raw fire-clay, which has been mixed with coarsely ground burnt clay from old crucibles or broken bricks of a previous heat, to reduce the shrinkage and distortion in the kiln. The pots used in glass making, and the fire-clay boxes (seggars, § 489) used in firing porcelain, are of the same general composition. Crucibles used in melting metals are of fire-clay mixed with flaky graphite, the latter being added to decrease the wear by erosion, and to retard oxidation.

487. Pottery.—Unglazed pottery resembles brick in being permeable to water, but the best grades are made of a purer clay, which burns to a light buff or white, or are at least surfaced with such material. (1) A great deal of pottery is still molded on the potter's wheel. This, one of the most ancient of human implements, is as old as civilization, and has been the object of independent invention by primitive modern tribes in many different parts of the world. (2) But much pottery is now formed by pressing into molds and (3) by pouring a thin clay suspension into plaster-of-Paris forms, which absorb the excess moisture. The changes that take place when pottery is burned in the kiln are the same as those that have been described for brick: **a *gradual dehydration*, accompanied by a shrinkage and loss of plasticity on the part of the clay; and eventually an actual *partial fusion* of the more readily melted constituents, forming a fluid which serves to cement the remainder of the material into a solid, stony mass.**

Pottery (glazed and unglazed) is produced in practically every state of the Union, but the two most important centers of the industry are in Southeastern Ohio and New Jersey. Ohio also produces great quantities of unglazed drainage tile and terra cotta, products identical in their chemical nature with ordinary unglazed pottery.

Pottery that has received a superficial glaze or enamel, to make it waterproof, is commonly termed *earthenware*. The cheapest and least effective of these glazes are those produced on roofing-tile and sewer pipe by throwing common salt into the kiln in which the ware is being fired. This, in the presence of moisture, at the high temperature there obtaining, reacts with the silica of the clay, to produce a fusible silicate; in principle:

$$2NaCl + H_2O + SiO_2 = Na_2SiO_3 + 2HCl \uparrow .$$

To produce white earthenware, it is necessary to employ a mixture of white-burning ball-clay and kaolin, with a little flint and feldspar. After firing, a glaze is applied by dipping the object in a thin suspension of powdered *frit* (a low-melting glass), with the addition of some white lead (§ 580) and flint. When the ware is reheated to a somewhat lower temperature than that reached in the first firing, this covering melts, forming a silicious glaze—a silicate of lead, sodium, and calcium. The more easily fusible glazes contain borates as well.

488. Chinaware and Stoneware.—The material known as **English chinaware,** or **bone china,** differs from any of those just described, and resembles porcelain in being completely non-porous; and, though it usually receives a coating of glaze or enamel, is not dependent on the same for imperviousness to water. It is molded from a mixture of bone ash (calcium phosphate) kaolin, and feldspar (about in the proportion 3 : 2 : 1). When this material is fired in a kiln, the bone ash and feldspar fuse to a certain extent, and fill up the pores between the particles of kaolin. The glaze, afterward applied in the same manner as described above for earthenware, is to improve the appearance of the surface, and prepare it for decoration in color.

Stoneware is a dense, heavy, non-porous ceramic material, used in the industries for pumps and piping for circulating acids. The ingredients are refractory clay, with a proportion of fluxing material, such as feldspar, to insure that the pores shall become completely filled with fluid at the unusually high temperature at which the ware is fired. Sometimes a vitreous glaze is applied in addition.

489. Porcelain.—The acme and perfection of the ceramic art is **porcelain.** This had its origin with the Chinese, who had long been accustomed to use pure white clays of low plasticity, and who fired their wares at higher temperatures than would have been possible with inferior raw material. The earliest products worthy of the name of porcelain probably date from about A.D. 900—a matter of six or seven centuries before the development of the art in Europe.

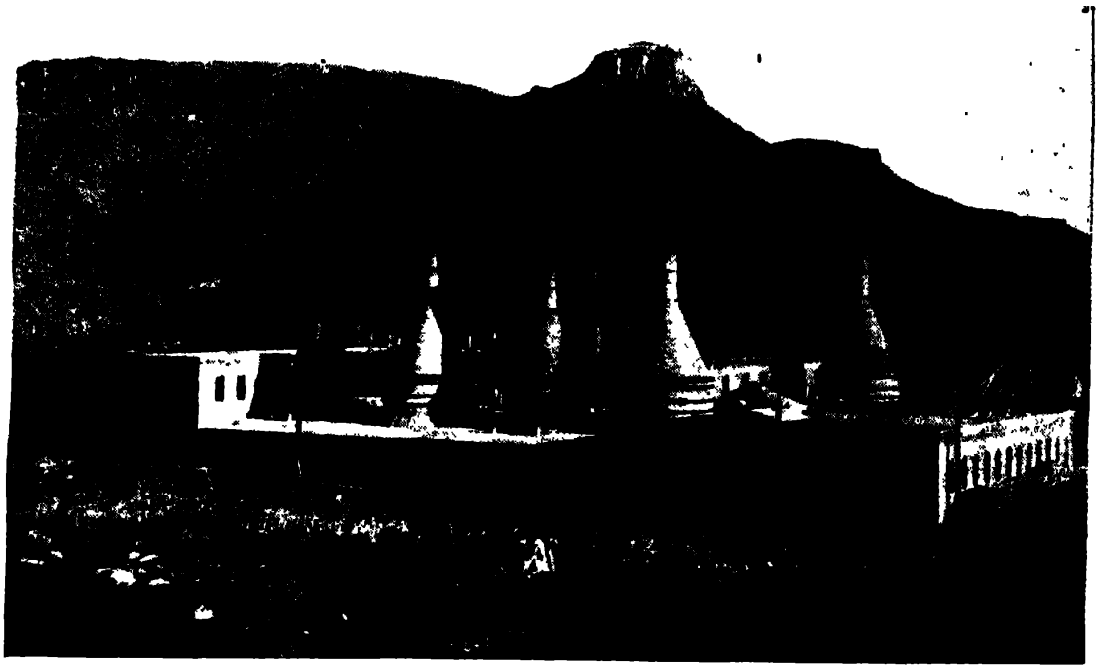

FIG. 109—A porcelain factory in Colorado. Note the conical stacks of the kilns in which the porcelain is fired.

The ingredients of porcelain are kaolin (§ 470), quartz, and powdered feldspar, in variable proportions. These are very carefully ground, floated in water, and the coarser material reground or discarded. The suspension thus obtained is put through filter presses to obtain a heavy paste. The plasticity of this is much less than that of the clays used in producing the best grades of white earthenware and chinaware; nevertheless, by keeping this material in storage for a period of several months, organic impurities ferment, and the kaolin appears to become more highly hydrated and plastic. The paste is then molded into the desired form, air-dried, placed in covered fire-clay boxes (**seggars**), and fired at a low red heat.

The final step is to cover the objects thus formed with a paste of kaolin, quartz, marble, and feldspar, and fire again.

The porcelain used in chemical laboratories must be capable of withstanding the action of acids and dilute alkalies, and more than commonly resistant to sudden changes in temperature. That used for electrical insulators, must have considerable mechanical strength, low shrinkage in firing, high electrical resistance, and imperviousness to moisture; but it need not have the white color and translucency demanded of decorative porcelain. It is really only a superior grade of stoneware.

FIG. 110.—Interior of an American porcelain factory.

To this product we owe the possibility of high-tension transmission of electrical energy to points remote from its source—trains hauled over the Rocky Mountains by the weight of water descending distant cascades, and cities illuminated by fires burning under boilers at coal fields hundreds of miles away. The United States, which leads the world in the electrical industries, produces enormous quantities of low- and high-tension insulators.

EXERCISES

1. What raw materials are employed in the preparation of each of the following: Glass, Portland cement, English china, porcelain. Outline the process of manufacture in each case.
2. Draw up a table, based on the present text and some reference work on

economic geology, of the physical and chemical characteristics of the principal industrial types of clay.

3. Explain the following terms: Enamel, refractory, terra-cotta, salt glaze, cobalt blue, alundum, emery.

4. What are the principal differences in methods of manufacture and physical properties between porcelain, stoneware, and earthenware?

5. Should a pigment to be applied under a transparent glaze, in decorating earthenware, be of lower or higher melting point than one applied over the glaze, and why?

6. Explain why a chemical analysis of a clay tells little of its chemical *composition*.

7. Explain how the character of silica as an acid anhydride is applied in the manufacture of artificial stone (§ 485).

8. Describe the casting of earthenware from thin clay suspension. Why is a little dilute alkali frequently added to the suspension, previous to casting (§ 390)?

9. To which are clay crucibles most resistant: acid or basic charges? Explain.

10. What kind of a material would you recommend in each of the following situations: Small crucible for melting steel; hearth for melting litharge (§ 577); condenser for a nitric acid still; evaporating basins for concentrating sulfuric acid on a commercial scale; mixing vats for the preparation of superphosphate fertilizer (§ 314).

CHAPTER XXXVIII

IRON AND STEEL

After aluminum, the most plentiful metallic element is iron. It betrays its presence everywhere, in many dark-colored minerals, and in the russet-brown, and buff of bricks, pottery, sandstones, clays, and soils. If all iron compounds had happened to be colorless, we should miss most of the pleasant tints of landscape and countryside. Blood, in addition, owes its red color to a compound of iron (§ 391.

Iron makes up about 4 per cent of the solid rocks of the earth's crust. Indeed, the magnetic properties of the planet and its high average density lend weight to the suspicion that its interior may be largely solid iron. Most of the meteorites that reach us from distant parts of space consist principally of this one element, commonly alloyed with nickel. The numerous lines of iron are found in the spectra of all the fixed stars of intermediate age, of which our own sun is an example.

Iron is the most useful of metals, partly because of its extreme abundance, but largely because of the ease with which its properties may be altered by adding small amounts of other elements, or by tempering or annealing (§ 499). According to its composition and previous history, it may be the toughest and strongest of metals, or one of the most brittle; highly magnetic, or almost completely non-magnetic; highly expansible with increasing temperature, or with a coefficient of expansion almost zero; so resistant to oxidation that it will withstand centuries of weathering or a long period of heating, or so easily oxidized that it catches fire of its own accord, like so much yellow phosphorus, when exposed to the air. At present, the world produces each year over 60 million tons of pig iron, which are partly included in the annual production of about 70 million tons of steel. This is more than twenty times the production of all the other metals combined.

490. Iron Ores.—To be useful as an ore, an iron mineral must contain at least 30 to 40 per cent of iron. By far the most important iron ore is **hematite,** or ferric oxide, Fe_2O_3 (the same as red ocher, or rouge, § 503). As much as 70 million tons of this have been mined in the United States in a single year (1917).

A somewhat hydrated form of this mineral, known as **limonite,** or bog iron ore, is often mined. Magnetic iron oxide, or **magnetite,** Fe_3O_4, is also important. In Europe a large quantity of **siderite,** or ferrous carbonate, $FeCO_3$, is smelted. Iron pyrite, FeS_2, consumed in enormous quantities in the manufacture of sulfuric acid (§ 240), is of no use as an ore of iron.

with the silicious impurities of the ore, to form a slag, consisting largely of calcium metasilicate, $CaSiO_3$.* Notice that slag-formation must not begin until after all the ore has been reduced to metal; otherwise, a large part of the iron would be lost by direct union of FeO with SiO_2 to form a slag of ferrous metasilicate, $FeSiO_3$.

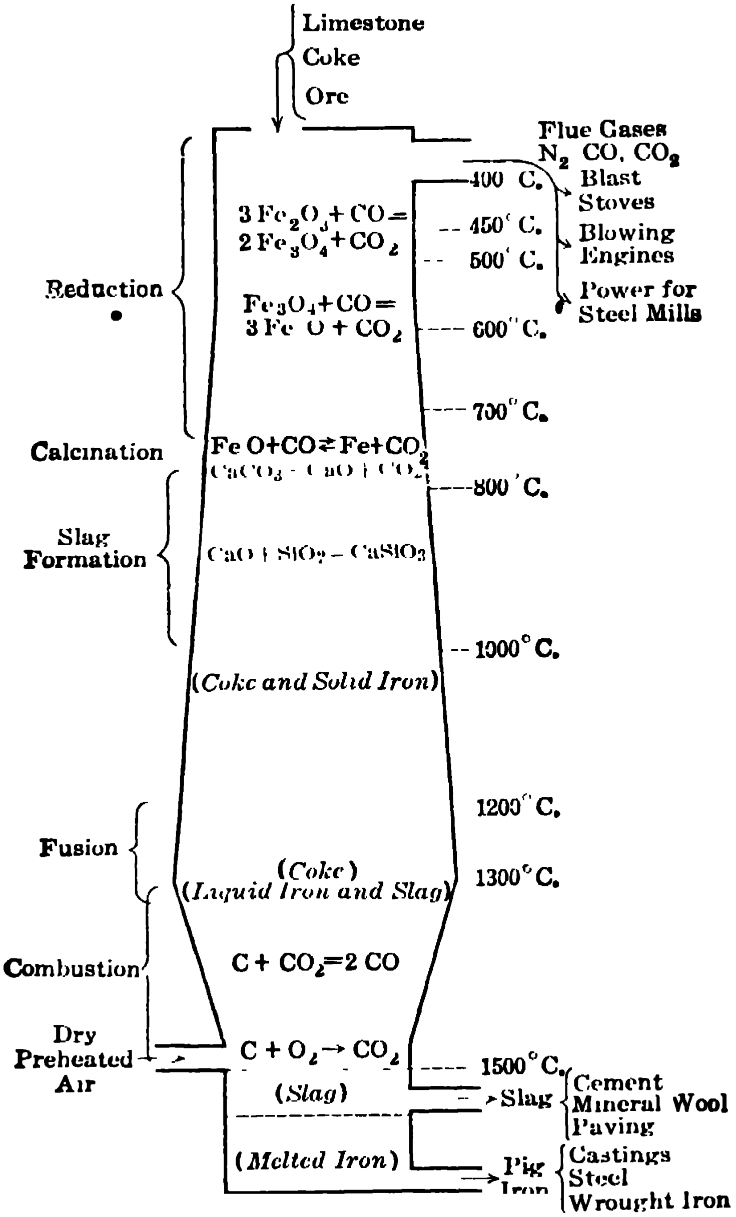

FIG. 112.—Reactions of the blast-furnace.

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* If the impurity present in the ore happens to be limestone, the flux used will be sand or feldspar. If the ore is quite pure, both sand and limestone must be added, to form enough slag to cover over the molten iron in the bottom of the furnace and prevent it from being oxidized.

(3) Just below the middle of the furnace, at its widest part, the temperature reaches and exceeds the melting point of cast iron. The reduced iron and slag both melt in this zone. The contraction of the furnace walls below this point is to allow for the decrease in volume due to fusion.

(4) At the level of the tuyeres, vigorous combustion takes place. Since air is present in excess, the first product of the combustion is CO_2. But as this passes upward through the overlying layer of white-hot coke, it unites with the latter to form CO, which serves for the reduction of the iron ore in the top part of the furnace.

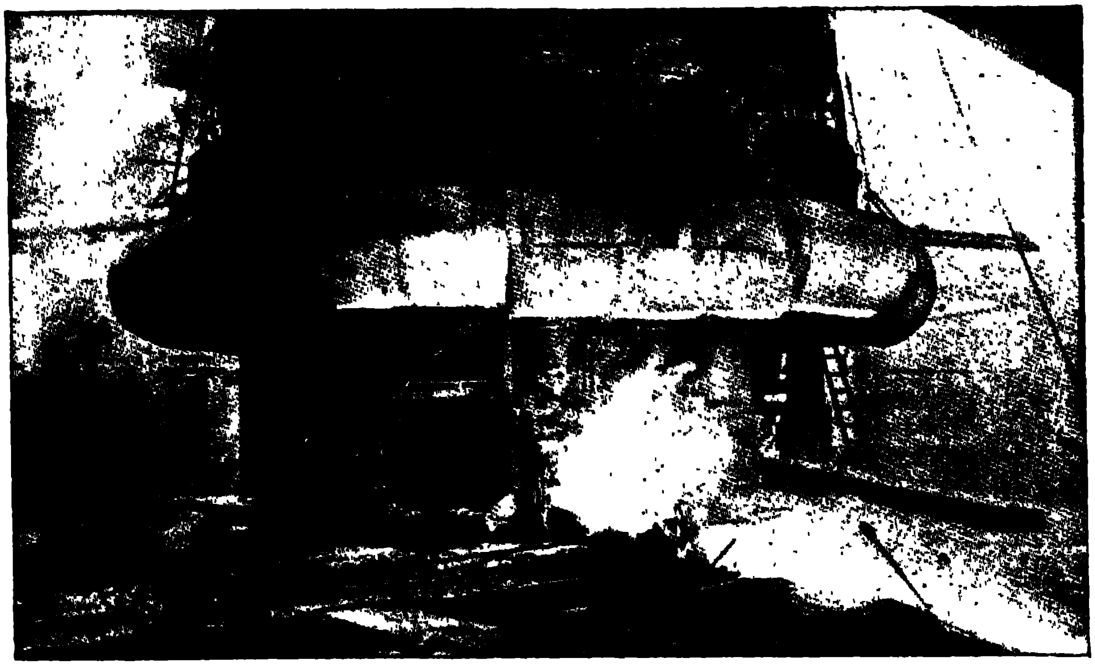

Fig. 113 —Tapping pig iron from blast-furnace.

If just enough CO were generated in the lower part of the furnace to reduce the iron ore above, it would all be oxidized back to CO_2 by the ore, and the only gaseous products escaping from the top of the furnace would be CO_2 and N_2. But actually a large excess of CO is always employed, because the reactions in the upper part of the furnace are reversible (§ 217).

493. Blast Furnace Products.—The main product of the blast furnace is **pig-iron,** an impure form of the metal containing **4 to 10 per cent of C and Si, with smaller amounts of Mn, S, P, and other elements.** These impurities lower the melting point of iron from 1530° to about 1130° C. (Compare §§ 99, 404.) Pig-iron has no very considerable *tensile strength*; i.e., it is very easily pulled apart by a direct strain. But its low melting point makes it valuable (when mixed with scrap iron) for casting stoves, steam radiators, window weights, and similar objects not subject to great tension or sudden shocks.

The most important by-product of the blast furnace is *blast-furnace gas*. This is generally somewhat more than half nitrogen, with the rest CO and CO_2, in about equal proportions.

The blast furnace is not merely a source of iron. It is the greatest gas-producer in the world. Some idea of the torrent of hot gas issuing from a furnace in operation may be obtained from the statement that a pipe 6 to 10 ft. in diameter is needed to carry it all away. A single furnace may furnish over a hundred million cubic feet of gas a day—enough to heat its own air blast in a series of great stoves, supply gaseous fuel to the tremendous blowing engines, and have plenty left over to furnish power for a neighboring steel mill, or a small town.

The **slag** produced by a blast furnace is commonly discarded; but it is put to occasional use for surfacing railroad embankments, or for making paving stone, mineral wool, or cement. In case it happens to carry an unusual amount of phosphorus it may be ground and sold as fertilizer.

A large blast furnace may require 1500 tons of iron ore in a day, 1000 tons of coke, 500 tons of limestone, and 4000 tons of air; it will turn out 1000 tons of pig iron every 24 hours, running continuously day and night for several years, until it finally needs to be shut down to renew the furnace lining.

494. Wrought Iron.—Iron, when melted, readily dissolves carbon, phosphorus, sulfur, and many other elements. Thus, the molten pig-iron produced by the blast furnace is very impure, and of a quality quite inferior to that of the spongy iron produced by more primitive methods of smelting. **The only advantage of the blast furnace is that it produces iron continuously, in liquid form.** If it did not do this, the furnace would have to be torn down after completing the reduction of a single charge of ore.

To improve the quality of pig-iron, it is purified by melting in a flat-bottomed **puddling furnace,** in contact with a bed of hematite or magnetic iron oxide.

Flames from burning coal, mixed with an excess of air, sweep over the surface of the iron, and presently melt it. The carbon, silicon, and phosphorus contained in the metal are oxidized by the excess of air and by the iron oxide of the furnace bed. The CO thus produced escapes. The SiO_2 and P_2O_5 unite with the magnesia lining of the furnace and with some of the iron oxide to form a basic slag, which floats on the surface of the molten metal. Sulfur is removed in this slag as ferrous sulfide. This purification raises the fusion temperature of the iron until the latter no longer melts freely, but gathers together in a pasty mass. It is then molded into large balls, which are removed from the furnace, worked under a steam-hammer, and passed under rollers to squeeze out the slag.

Iron produced in this way is called **wrought iron.** It is far tougher and more flexible than pig-iron, has almost the tensile strength of steel, and is easily welded, drawn into wire, or worked on the blacksmith's anvil. It is used for chains, bolts, anchors, and wire-fencing. Being nearly pure iron, it has a melting point much higher than that of pig iron. It is thus commonly used for grate-bars. **Mild steel** is a wrought iron to which has been added several tenths of a per cent of carbon, to increase its tensile strength. Explanation, § 499.

If a piece of wrought iron is cleaned and examined under a microscope it will be seen to have a fibrous structure, somewhat like wood, and to be crossed with wavy streaks of dark material, due to slag not completely removed by the rolling process. Cast iron and steel, on the other hand, show a crystalline structure.

495. High-Carbon Steel.—**To convert pig-iron into steel, the impurities present in the former must be removed and definite percentages of carbon and manganese added.** This result may be accomplished in a number of different ways.

(1) **Cementation Steel.** Wrought iron is heated to redness, in a closed box, in contact with powdered charcoal. The carbon diffuses into the solid iron, changing it into steel. This process is now of very little importance.

(2) **Crucible Steel.** Wrought iron, or a very pure grade of open-hearth steel, is melted in a graphite crucible, and enough cast iron or charcoal added to give it about 0.75 to 1.50 per cent of carbon. Either the cementation or the crucible process produces what is called " high-carbon " steel or hard steel. It is employed for razors, knives, and wood-working tools, for it is tough and retains a cutting edge very excellently.

496. Bessemer Steel.—This process was invented in 1852, by Kelly, an American, and perfected by Bessemer, an Englishman. It takes place in two stages: first, the impurities are burned out of molten pig-iron by a blast of air; second, definite amounts of carbon and manganese are added.

The method makes use of a special apparatus called a **Bessemer converter** (Fig. 114). This is a pear-shaped vessel, about 15 ft. in height, built of boiler plate, and lined with silicious material (sand, with a very little clay). The converter is turned on its side, and 10 to 20 tons of molten pig-iron, taken directly from the blast furnace, poured into it. Compressed air is then turned on, entering through the horizontal, hollow trunnions on which the vessel is pivoted, thence passing to a set of small openings in the bottom. As the converter is brought back into an upright position, the air streams up through the molten iron, burning the silicon to SiO_2, the manganese to MnO, the carbon to CO, and a part of the iron to FeO. Phosphorus and sulfur are not removed in the American Bessemer process.

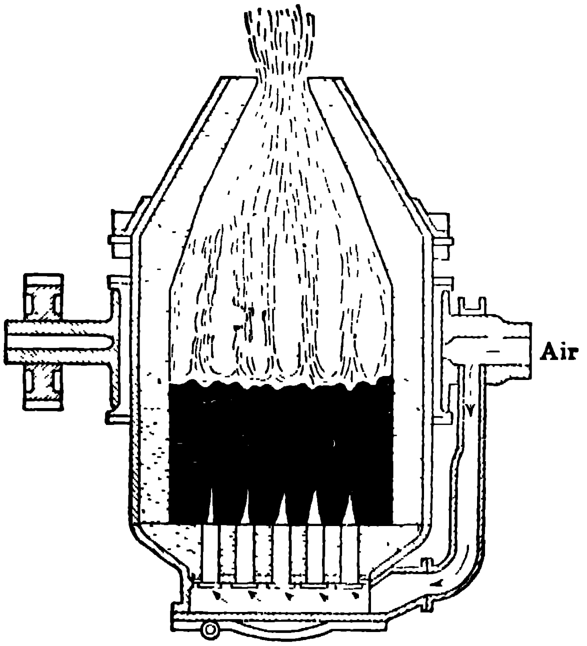

Fig. 114.—Cross-section of a Bessemer converter

The heat given off in this process of combustion is sufficient to raise the temperature of the molten iron several hundred degrees, and to keep it fluid in spite of the fact that its melting point is raised by the process of purification. The oxidation of the impurities is marked by a great torch of burning carbon monoxide, issuing from the mouth of the converter. After a few minutes this suddenly dies away. Next, some *spiegeleisen* is added—an alloy of iron, manganese, and carbon. The two latter elements reduce any FeO that may have been formed, and any excess left over dissolves in the molten iron to convert it into steel.

Very frequently, some *iron-titanium*, *iron-vanadium* or *iron-silicon* alloy (§ 410), or some metallic aluminum is added to the finished steel. Aluminum and silicon act as **scavengers**, reducing any CO dissolved in the metal to carbon, thus yielding steel that produces castings freer from defects due to enclosed bubbles of gas. Titanium and vanadium will remove *air*, for they combine directly, both with oxygen and nitrogen. The scavenger elements are, of course, oxidized, separate as slag, and need not be found in the finished steel.

Bessemer steel can be produced very cheaply, for the whole process can be completed in less than half an hour, and each charge may yield as much as 20 tons of steel. This one invention, perfected just before the American Civil War, cheapened steel enormously, and enabled the western part of the continent to be spanned by railroads and developed with extraordinary rapidity during the ensuing half century.

Now, however, ores free from sulfur and phosphorus are not so easily obtained; and, furthermore, Bessemer steel, with the best of precautions, is likely to produce defective rails, due to enclosures of gas. Our modern heavy locomotives, pulling long freight trains, and high speed passenger transportation—the famous "Twentieth Century Limited"—were thus only possible when Bessemer rails had given place to those made by the open-hearth process. At present, Bessemer steel is restricted to structural frameworks, concrete reinforcement, and similar purposes, in situations where it is not exposed to continued vibration, sudden shocks, or active corrosion.

FIG 115.—The chemical laboratory of a steel works. The iron ore, pig iron, and steel are carefully analyzed at each stage of the process of manufacture This photograph shows a set of electrically-heated combustion furnaces (§ 77) for burning samples of steel in a current of oxygen, to determine the percentages of carbon they contain. At the right are cylinders of compressed oxygen.

497. Open-Hearth Steel.—In the open-hearth (or Siemens-Martin) process, pig-iron is melted with steel scrap and iron ore, on the hearth of a shallow furnace (Fig. 116) lined with **silica brick** (***acid process***) or with **lime and magnesia brick** (***basic process***). The fuel is producer gas.

It is necessary to preheat both the air and the gas used in firing the furnace in order to secure a temperature high enough to keep the steel melted during the final stages of its purification. This heating is accomplished by a regenerative system, consisting of four large chambers (*A*, *B*, *C*, *D*, Fig. 116) filled with a checkerwork of silica brick. At the start, the brickwork in *A* and *B* is heated to incandescence. Then gas is passed through *A* and air through *B*, and both air and gas are thus raised to a high temperature before they mingle and combine within the furnace, *F*. The intensely hot flame thus produced sweeps down over the charge of pig-iron, steel scrap, and ore, thence out through the chambers *C* and *D*, raising the checkerwork in the latter to a white heat. After a little while, *A* and *B* have given up so much of their heat to the incoming gas and air that the current needs to be reversed. Air and gas then enter through *C* and *D*, which have meanwhile been heated, while the products of combustion sweep out through *A* and *B* and reheat the checkerwork they contain.

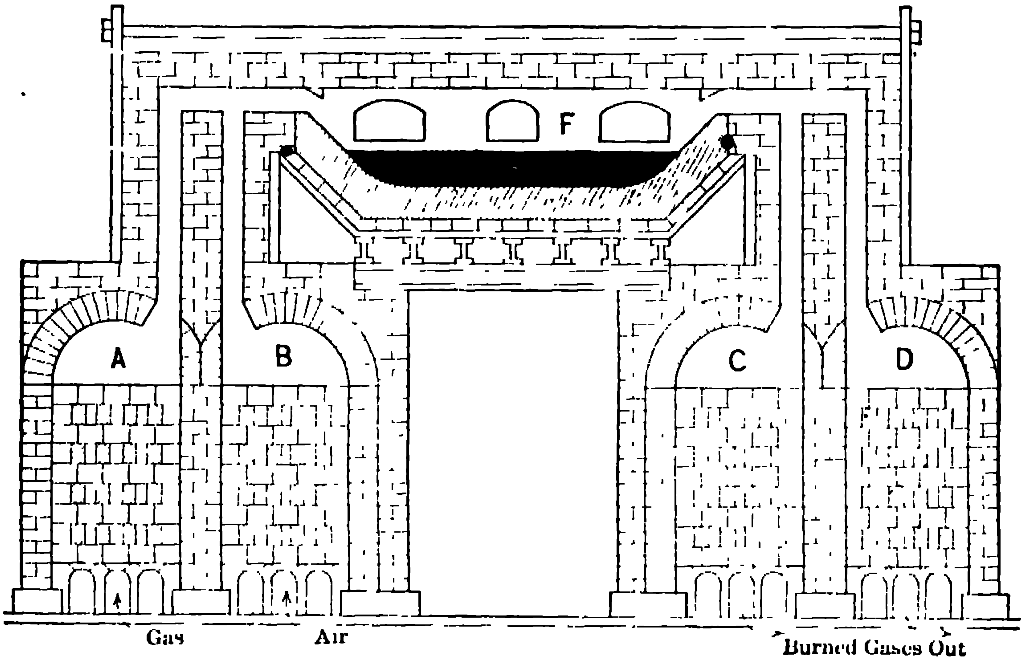

FIG 116 —Cross-section of an open-hearth furnace

The molten material within the furnace is gradually purified by reaction with the iron ore. Silicon is oxidized to SiO_2, and slags away as a calcium-ferrous-magnesium silicate. Carbon is removed as CO. Sulfur and phosphorus are again unaffected, unless the furnace is lined with basic material (CaO, MgO); but in the latter case both sulfur and phosphorus are oxidized and removed as calcium and magnesium sulfates and phosphates. In the end, the properties of the steel may be modified by the addition of a definite quantity of **spiegeleisen or high-carbon steel.** It is customary to add some **aluminum or ferro-titanium** as the steel is drawn from the furnace, to remove dissolved gases.

The great advantage of the open-hearth process is that chemical changes proceed in a very leisurely fashion, under close control, during a period of eight to ten hours. The steel is drawn from the furnace only when chemical analysis shows it to have precisely the composition desired. What the open-hearth furnace lacks in speed it largely makes up in capacity. As much as 125 tons of steel can be produced in a single melting, as compared with a maximum of 20 tons for a Bessemer converter.

As late as 1907, the Bessemer and open-hearth processes produced about equal quantities of steel; but at the present time the open-hearth produces almost 80 per cent, the Bessemer process only about 20 per cent, and all other processes together less than 1 per cent of the total annual American production of about 50 million tons of steel—almost three-fourths of the world's production. Open-hearth steel is now used almost exclusively for heavy rails, bridge girders, armor plate, and other products subject to *sudden strains*, but demanding cheaper production than is possible with the electric process next to be described.

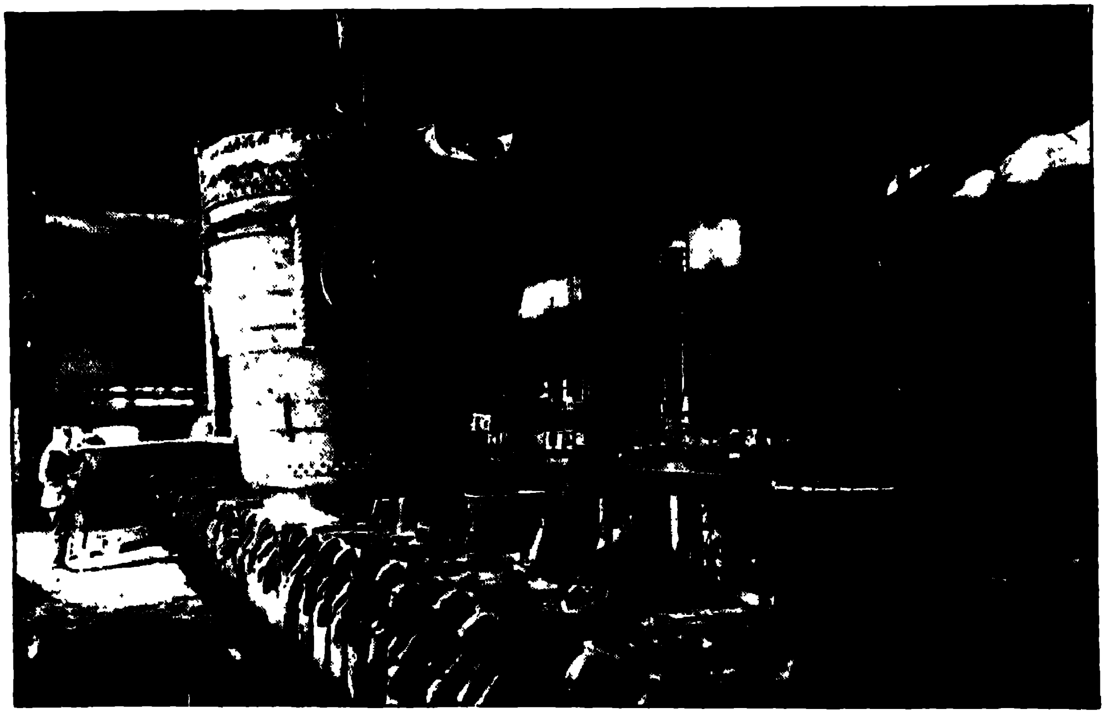

FIG. 117.—Pouring molten steel from ladle into ingot molds. Open-hearth furnaces in background.

498. Electric Steel.—Where a very tough, strong grade of steel, of absolutely dependable quality, is required—as in the manufacture of automobile engines, transmission systems, axles, and wheels—the **electric furnace** is pressed into service. This permits an even **more careful and deliberate adjustment of the chemical composition of the finished product** than is possible with the open-hearth method. A further advantage is that **the operation is con-**

ducted in a non-oxidizing atmosphere. Finally, the temperature is much higher than can otherwise be obtained, and certain ferro-alloys are so infusible that they can be prepared in no other way. The materials thus made available for refining secure a more complete removal of sulfur and phosphorus—the two most objectionable impurities in steel—than is possible by any other method.

About half a million tons of steel are prepared in the United States each year in electric furnaces of the type shown in Fig. 118. These are lined with a mixture of basic slag and magnesia. The charge is 15 or 20 tons of Bessemer steel, taken directly from the converter. Enough basic slag is placed on top of the charge to cover the steel and exclude air. Two or three enormous graphite electrodes—2 ft. in diameter and 10 ft long—are lowered through the cover of the furnace until they touch the layer of molten slag, and are then slightly withdrawn.

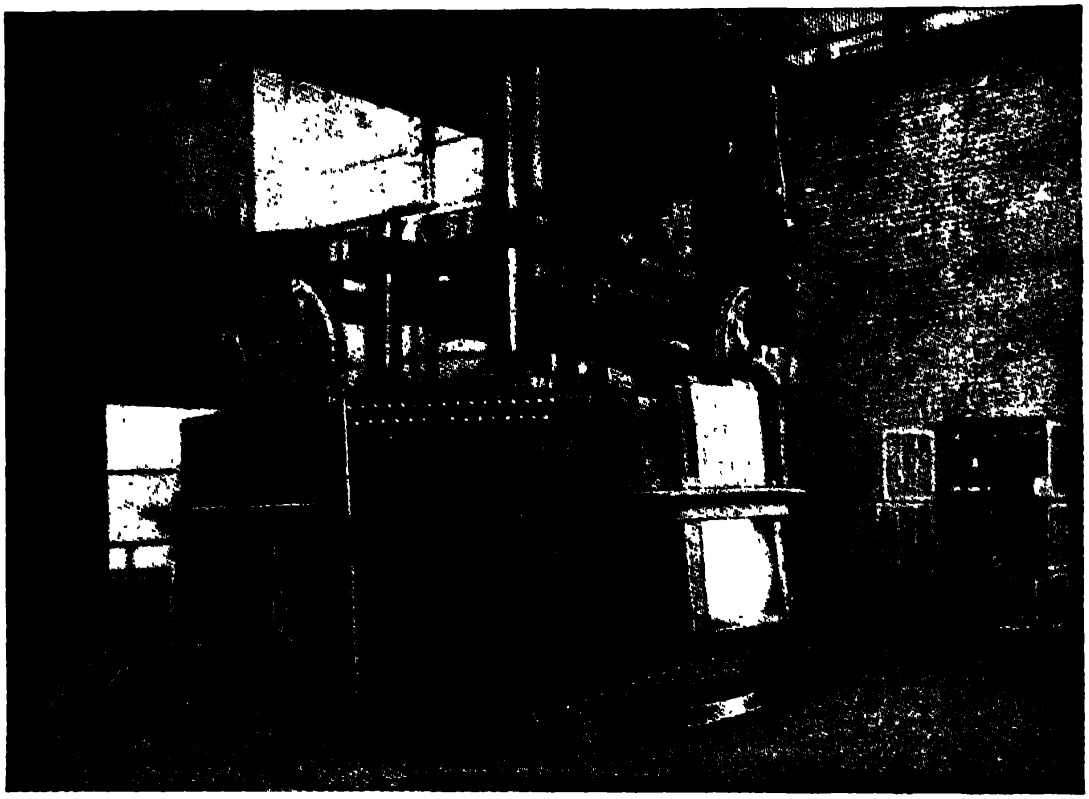

FIG. 118.—An electric steel furnace.

499. Annealing, Hardening, and Tempering.—Iron, like carbon, sulfur, phosphorus, and many other elements, exists in different allotropic forms, having distinct physical properties. The ordinary form of iron, the principal constituent of wrought iron, is soft, ductile, easily magnetized or attracted by a magnet.

It is called **α-ferrite.** When this is heated it passes through two different transformations, and above 920° becomes **γ-ferrite,** which is denser, and non-magnetic.

Now γ-ferrite can dissolve and retain up to about 2 per cent of carbon, as a homogeneous solid solution (§ 91) which goes under the name of **austenite.** **But *α-ferrite*, the form of iron stable at ordinary temperatures, is unable to dissolve carbon,** and if any of the latter element is present in the beginning it will crystallize out as the temperature slowly falls, in the form of an iron carbide, Fe_3C, called **cementite.**

The properties of steel, therefore, depend both on its chemical composition and its previous history—whether it has been cooled slowly or rapidly from a higher temperature. **In the case of slow cooling, there is time for separation of crystals of cementite.** Thus, heated steel containing about 1 per cent of carbon remains homogeneous (**austenite**) until the temperature has fallen to about 725°. It then begins to segregate; and, if the cooling is sufficiently slow, will presently be transformed completely into a crystalline ground mass called **pearlite,** with scattered areas of cementite, Fe_3C.

Steel which has thus been heated to a bright red heat and then slowly cooled is said to have been **annealed.** If it is not too coarsely crystalline, it will then have a considerable degree of softness and pliability, due to its chief constituent, α-ferrite. It will resist wear better than pure wrought iron, on account of the presence of crystals of a somewhat harder material, cementite.

If a steel is heated to bright redness and then cooled very suddenly, as by quenching in water or oil, it is **hardened.** The separation into α-ferrite and cementite does not have time to take place before the temperature has fallen so low as practically to arrest further movement of the atoms. The homogenous structure of austenite * is retained to the very end; and we have a product which is hard and brittle, partaking somewhat of the quaiities of glass, itself a similar supercooled liquid, or solid solution.

Tempering consists in reheating such a sample of hardened steel to a lower temperature, much below redness (200° to 350°), in order to encourage crystalline growth, or permit a partial separation of cementite, or perhaps relieve the mechanical strains that are always set up on sudden cooling. The sample may thus be given any desired degree of hardness, intermediate between that of fully hardened and that of fully annealed steel. If the percentage of carbon in the steel is known, the general appearance of a brightly polished specimen, when examined with the microscope, will usually disclose the kind of heat treatment to which it has been subjected, and its most important properties.

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* Austenite is regarded as a *solid solution* of cementite in γ-ferrite. Under the microscope, the solid solution is shown to exist in several conditions, which are called *austenite*, *martensite*, *troostite*, and *sorbite*. It would take us too far into the field of *Metallography* to attempt to distinguish between these different metallographic constituents of steel, and the term *austenite* will be used, somewhat erroneously, to signify any solid solution of cementite in iron.

Wrought iron cannot be hardened or tempered, because it contains almost *no carbon at all.*

In pig-iron, part of the carbon is present in solid solution (austenite) and the excess as graphite. White cast iron is a nearly homogeneous solid solution, and is accordingly hard and brittle. Gray cast iron, on the other hand, is softer and more malleable, because some of the carbon (with slower cooling) has separated as flakes of graphite, leaving a ground-mass of relatively pure iron.

500. Case Hardening.—Whatever steel gains in *hardness* it loses in *ductility*. It cannot well have the qualities of supercooled austenite and pure ferrite, both at the same time. Thus, in fashioning such articles as axles for railroad cars, we find ourselves in a dilemma: strength and a certain degree of flexibility are needed, for without these qualities the axle will be broken by the continual violent jolting; but the bearing surfaces, where the axle passes through the wheels, must be hard, or they will be worn away very rapidly.

The difficulty is met by using a strong and flexible mild (low-carbon) steel, which is given a very thin coating of hardened (high carbon) steel, by heating in a closed box containing charcoal, and afterward quenching in oil. The process is called **case-hardening.** A certain amount of barium carbonate is generally mixed with the charcoal; on being heated, this liberates CO_2, which then reacts with the hot carbon to form CO (§ 334).

It is *carbon monoxide*, and not carbon itself, which is the real hardening agent. This penetrates the hot steel to a certain distance, and reacts with the iron to form cementite:

$$2CO + 3Fe \rightleftarrows Fe_3C + CO_2.$$

Since the reaction is reversible, the amount of cementite produced will depend on the concentration of CO available at any given distance from the surface. Actually, the altered layer rarely exceeds the thickness of a sheet of paper.

501. Alloy Steels.—In **simple steels,** the only elements alloyed with the iron are carbon and manganese (up to about 1.5 per cent of each). Phosphorus and sulfur should be less than 0.05 per cent each, as the former causes the steel to be brittle at room temperatures and the latter at redness. **Alloy steels** are made by the addition of other elements (or a high percentage of manganese) to simple steels. But if scavenger elements, such as Al, Si, Ti (§ 496), are added only in the amounts needed to remove dissolved gases, these elements are not found in the finished material, and the latter is not counted as an alloy steel.

The properties of the alloy steels depend quite as much on *heat treatment* (hardening, tempering, and annealing) as on *chemical composition*. It is accordingly incorrect to state that one element produces a given effect on the mechanical properties of steel, and another element a different effect. In most cases, a desired result can be obtained with several steels of widely different composition, by using the heat treatment proper to each.

Manganese steel contains 11 to 14 per cent of manganese. It is almost completely non-magnetic, in spite of the fact that it contains nearly 90 per cent of iron. When quenched in oil from a temperature of about 1000° C., it becomes remarkably hard and tough, and very resistant to wear. It is used for railroad rails on curves, steam shovels, buckets for hoisting machinery, and the like. Its employment for such purposes on the Panama Canal shortened that work by years, and saved many millions of dollars.

Chromium steel contains 1½ to 2 per cent chromium. When annealed, it has much the same properties as manganese steel, but is more resistant to deformation by pressure. It is used for the jaws of rock crushers, and for ball bearings, safes, and files.

Nickel steel usually contains about 0.25 per cent carbon and 2 to 4 per cent nickel. It has a greater tensile strength than simple steel, and resists corrosion better. It is used for wire cables, propeller shafts, bridge trusses, and bicycle frames. When the nickel is raised to 30 to 40 per cent, the steel becomes almost as rust-resistant as monel metal (§ 525), and is used for pumps and valves for salt-water mains. A 36 per cent nickel steel, called **invar**, having a coefficient of expansion scarcely more than zero, is used for pendulums and surveyors' tapes.

Nickel-chromium steel contains these two elements in about the proportions in which they are used separately. By suitable heat treatment, this steel may be given a wide range of toughness, hardness, tensile strength, etc. It is used for automobile parts, projectiles, armor plate, masts and spars.

Chromium-vanadium steel contains about 1.0 per cent chromium and 0.15 per cent vanadium. It can be given the toughness of nickel steel, but has greater ductility, and can be bent double, when cold, without breaking. It is a favorite for manufacture of automobile frames and axles.

Silicon steel (1 to 5 per cent Si) is less easily broken by flexure than most steels of conspicuous hardness. It is used for automobile springs and hacksaw blades. Its most important use is in electrical transformers, on account of the small amount of energy lost in its magnetization and demagnetization (low hysteresis). For ferro-silicon, see § 415.

Tungsten steel (0.6 per cent C and 6 per cent W) is used for permanent magnets in small electrical generators and electric meters (high magnetic retentivity). The famous " Damascus blades " of the Saracen Empire contained tungsten.

Chromium-tungsten steel contains about 0.75 per cent C, 4.0 per cent Cr and 17 to 20 per cent W. Its hardness is no greater than that of good simple steel; but it is better suited for automobile valves and lathe tools, for it will retain its hardness or cutting edge even when raised to a red heat. This is presumed to be due to the formation of a hard carbide of tungsten and chromium, stable at high temperature.

Various other alloy steels are occasionally used. Molybdenum, formerly a constituent of tool steels, is now chiefly used as a substitute for chromium-vanadium. Cobalt finds some use in tools for working some alloy steels that are too hard to be turned with ordinary tools. Pyrophoric alloys (§ 588) contain iron and cerium.

502. Why Iron and Steel Rust.—The most serious defect of iron or steel is its liability to rust and corrode. The rate of destruction by rust and corrosion varies greatly with the composition of the material and the conditions under which it is exposed. Wrought-iron pipes and nails have occasionally remained buried in moist earth for two or three centuries without much corrosion; but other samples, under apparently similar circumstances, have disappeared in a few weeks. Here is a problem worth careful study, for the total loss due to rusting, in the United States alone, probably amounts to several hundred million dollars each year.

The nearly pure iron prepared by electrolysis of a boiling solution of ferrous sulfate will not rust if hung in pure distilled water. Ordinary iron will not rust in a dry atmosphere, or in the absence of oxygen, and will rust but slowly in the absence of carbon dioxide.

From the standpoint of the electronic theory, the rusting of iron can be outlined in a very simple way:

1. Objects exposed to air are always covered with an invisible film of condensed moisture, even though the air is not saturated.

2. Iron is above hydrogen in the electrochemical series, and accordingly tends to lose electrons, and enter the solution as ferrous ions. But if it is homogeneous, and if air is absent, an equilibrium is reached as soon as a very small quantity has dissolved:

$$\begin{array}{l} \mathrm{Fe + 2H^+ \rightleftarrows Fe^{++} + 2H} \\ \qquad\qquad\qquad\qquad\ \ \updownarrows \\ \qquad\qquad\qquad\qquad\ \ \mathrm{H_2} \end{array}$$

3. If there are foreign particles (graphite) in the iron, or even if it is mechanically strained, different parts of the surface hold

electrons with different degrees of tenacity. They therefore cannot all be in equilibrium with the solution at the same time. Some parts of the surface lose electrons or act as anodes; while others act as cathodes (§ 424). Thus we have an *electrolytic process*, favoring corrosion.

4. Finally, if air is present, the ferrous iron which has been brought into solution is partly oxidized to the ferric condition;

$$4Fe^{++}+O_2+2H_2O \rightarrow 4Fe^{+++}+4OH^-.$$

It will be noticed that this reaction tends to make the solution less acid. Thus, in the end, a precipitate is formed, of an extremely variable composition, consisting of a mixture of ferrous hydroxide, ferric hydroxide, and basic ferrous carbonate. In this way, equilibrium is prevented, and corrosion continues, as long as moisture and oxygen are both present. Moreover, a little rust. once formed, tends to hold moisture, and thus accelerates corrosion.

503. Protection against Rusting.—The preceding statements indicate the nature of the measures that may be taken to protect iron or steel against rusting:

1. The metal should be of uniform composition, homogeneous, and free from mechanical strains.

2. It should be protected against stray currents of electricity.

3. If its surface is bare it should not be in direct contact with carbon, copper, tin, or any other element below iron in the electrochemical series. On the other hand, if it is in contact with zinc or aluminum, all the corrosion will fall on these two metals. This principle is sometimes employed in protecting boilers (§ 460).

4. Water that is to be passed through iron pipes becomes less corrosive if its dissolved air is first removed, by heating, or otherwise.

5. Where the cost is not too great, steel may be made more resistant to corrosion by alloying with nickel (§ 501). A few hundredths of one per cent of copper is a protection to sheet steel, for reasons not yet well understood.

6. Where permissible, the surface should be covered with a water-tight coating. This must be in actual contact with the iron, if the film of moisture responsible for corrosion is to be

excluded. It follows that the surface to be protected must be thoroughly cleaned, and free from rust.

The protective coatings commonly used on iron and steel fall into four classes:

1. *Paints, varnishes,* and *lacquers.* Some common paints for iron and steel are asphalt; linseed oil and red lead (§ 578); ocher (=ferric oxide, § 490); graphite paint; vaseline or lubricating oil.

2. *Enamels.* These are usually highly fusible glasses, containing boric oxide.

3. *Metallic coatings.* Nickel and copper are deposited on the iron or steel surface by electrolysis; zinc, lead, aluminum and tin, by dipping iron in a molten bath of the other metal. Zinc lies above iron in the replacement series, and serves as an absolute protection to the iron, as long as any part of the surface of the latter remains covered. Tin and lead lie below iron; and if the covering is perforated at any point, the iron beneath behaves as an anode, and corrosion there may go on faster than if the iron were entirely bare.

4. Coatings produced by alteration of the surface of the iron itself. Sometimes the metal is given a closely adherent black film of magnetic iron oxide, by exposing it to superheated steam (*Russian iron*). In the Parker process, the steel is dipped for a short time into a boiling, strongly alkaline, solution of sodium phosphate. This covers the surface with an almost invisible gray coating, presumed to be a basic iron phosphate. Rifles are commonly treated in this way; and many typewriter and automobile parts are so treated previous to enameling.

A similar invisible coating, of a very temporary nature, may be obtained by dipping sheet iron into concentrated nitric acid. A violent action takes place for a few moments, then suddenly stops. If the metal is then gently rinsed in a plentiful supply of water, it is found to be *passive:* it will no longer dissolve in dilute acids, and will precipitate copper from copper sulfate solution only very slowly. That this protection is due to a superficial coating is shown by the fact that the passivity may be destroyed by a sharp blow or by scratching. It is presumably caused by a layer of adsorbed oxygen, perhaps but one atom deep, over the entire surface of the metal.

504. Ferrous and Ferric Salts.—Ferrous salts are usually greenish, and dissolve to form almost colorless solutions. Ferric salts are reddish and dissolve to form yellowish solutions.

Ferrous salts can be oxidized to the ferric condition by nitric acid, chlorine, or bromine; or by potassium dichromate and permanganate in the presence of an acid:

$$FeCl_2+HNO_3+HCl \rightarrow FeCl_3+H_2O+NO;$$

$$FeSO_4+Br_2+H_2SO_4 \rightarrow Fe_2(SO_4)_3+HBr.$$

Balance by the method of § 135. Formulate also in terms of ions.

Ferric salts can be reduced to the ferrous condition by hydrogen sulfide, stannous chloride, nascent hydrogen, or metallic iron:

$$Fe_2(SO_4)_3+H_2S \rightarrow FeSO_4+S+H_2SO_4;$$

$$FeCl_3+Fe \rightarrow FeCl_2.$$

Balance. Formulate also in terms of ions.

Ferric salts are more readily hydrolyzed than ferrous salts; **for $Fe(OH)_3$ is a less active base than $Fe(OH)_2$.**

Ferrous iron is detected by the fact that it gives a blue color with potassium ferricyanide, $K_3Fe'''(CN)_6$. **Ferric iron** gives the same blue color (**Prussian blue**) with potassium ferrocyanide, $K_4Fe''(CN)_6$. Note that **each species of iron is tested for by the use of a reagent which itself contains iron, but of the other valence.**

A still more delicate reagent for ferric iron, in the absence of nitric acid, is potassium sulfocyanate. This develops the intense red color of **ferric sulfocyanate** (or **thiocyanate**):

$$FeCl_3+3KCNS=Fe(CNS)_3+3KCl.$$

505. Some Compounds of Iron.—*Ferrous sulfate*, $FeSO_4 \cdot 7H_2O$, is occasionally used instead of alum for clarifying water. It is employed to some extent as a weed killer, and as a mordant in dyeing. It is a constituent of most of the writing fluids that write blue and turn black. This change is due to oxidation by the air The ferric salt thus produced then reacts with tannic acid present in the ink to form black ferric tannate.

Ferric alum, $KFe(SO_4)_2 \cdot 12H_2O$ is occasionally used as a substitute for ordinary alum, an aluminum salt of corresponding formula.

Potassium ferrocyanide (§ 338) $K_4Fe(CN)_6$, is made by fusing potassium carbonate with iron filings and nitrogenous material (dried blood, hair, or leather scraps). When the product is extracted with water, and the extract evaporated, the salt separates as beautiful lemon-yellow crystals (yellow prussiate of potash). It is almost non-poisonous in spite of its content of cyanogen. It is used for the preparation of potassium cyanide and in case-hardening (§ 509); and in the laboratory as a test for *ferric* iron.

Potassium ferricyanide, $K_3Fe(CN)_6$, is made by oxidizing potassium ferrocyanide with chlorine. It crystallizes in red prisms (red prussiate of potash), and is **intensely poisonous.** It is used in the preparation of blue-print paper and in the laboratory as a test for *ferrous* iron.

Blue-print paper is made by treating one side of any tough, well-sized paper with a mixture of ferric ammonium citrate and potassium ferricyanide. Light causes the ferric iron of the ferric ammonium citrate to be reduced (the citrate radical being oxidized). The ferrous iron thus produced at once reacts with the potassium ferricyanide to form a blue precipitate.

EXERCISES.

1. What percentage of iron is contained in an iron ore, containing 40 per cent hematite and 60 per cent limestone?

2. What weight of quartz is needed to slag off the gangue in the preceding ore, assuming the only product to be calcium metasilicate.

3. What are the chief differences in chemical composition, physical properties, and uses between pig iron and wrought iron? Between mild steel and hard steel?

4. Write and balance equations for:

(*a*) Reduction of hematite in several successive stages.

(*b*) Slag-formation in a blast-furnace.

(*c*) Reactions taking place in a blast-furnace.

(*d*) Removal of carbon from pig iron, in the production of wrought iron.

(*e*) Deoxidation of steel by a manganese-iron alloy.

(*f*) Removal of dissolved carbon monoxide from open-hearth steel by metallic aluminum.

5. How is wrought iron converted into steel? Explain what happens when hardened steel is annealed.

6. Explain case-hardening. Calculate the percentage of carbon in cementite.

7. Explain why surveyors' tapes rarely rust; and when rust does develop it usually appears where the tape has been spliced, or around one of the rivets used to mark distances.

8. Four strips of iron are half coated, respectively, with zinc, tin, lead, and copper. Which will rust more rapidly and which less rapidly than similar sheets of bare iron, when submerged in water. Explain. When rusting takes place show the direction of transfer of electrons through the metal.

9. Name three different advantages to be obtained by the use of nickel steel in boiler tubes.

10. Specifications for an eaves gutter state that it shall be of sheet zinc, free from cadmium; that the individual lengths shall be connected by crimping, and not by soldering; and that strips of waterproof wood or fiber shall be placed between the under surface of the zinc and the supporting iron brackets. Explain the need for these precautions.

11. Would you expect a sample of hardened steel to be more or less subject to corrosion after annealing? Explain.

12. What kind of special steel do you think would serve best in each of the following situations? Shaft for a steam turbine; recoil springs for a machine gun, needle for a mariner's compass, chains to travel through a furnace in an automatic stoker, drum for a concrete mixer, razors, rivets.

13. What successive steps are necessary in converting pyrite into ferrous sulfate, on a laboratory scale? Write and balance equations.

14. What successive steps would you use in converting metallic iron into ferric alum, on a laboratory scale. Write equations.

15. How, and under what conditions, do the following act upon iron? What are the products in each case? Water, copper sulfate, dilute sulfuric acid, concentrated sulfuric acid, aqua regia, chlorine, sulfur, carbon.

16. Write and balance equations for the oxidation of ferrous sulfate to ferric sulfate, in the presence of sulfuric acid, by potassium permanganate and potassium dichromate, respectively.

CHAPTER XXXIX

CHROMIUM AND MANGANESE

Since iron is in the eighth, or transition, group of the periodic table, the elements which it most closely resembles are found in adjacent positions in *the same horizontal row* of the periodic table, rather than in the same vertical column (§ 411). Its nearest relatives are, in fact, chromium and manganese on the left, and cobalt and nickel on the right:

Group	VIB	VIIB	VIIIB		
Element	Cr	Mn	Fe	Co	Ni

CHROMIUM

506. Occurrence and Metallurgy of Chromium.—The most useful chromium ore is **chromite** or **chrome iron ore, $Fe(CrO_2)_2$,** otherwise written as a combination of ferrous and chromic oxides, $FeO \cdot Cr_2O_3$.* Most of the small amount of chromite mined in the United States comes from California and Oregon. The most important deposits are found in British South Africa, Portuguese East Africa, New Caledonia (a large island lying northeast of Australia), and Greece. Small amounts of chromium are found in a great many other minerals, and are responsible for the red color of the ruby (essentially Al_2O_3), as well as the green color of the emerald (a beryllium aluminum silicate, § 585).

Most of the metallic chromium used in the industries comes upon the market as **ferrochrome,** an iron alloy containing about

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* This formula is really based upon the old-fashioned dualistic theory that salts are compounds of basic oxide (FeO) with acid anhydride (Cr_2O_3). Since Cr_2O_3 is more basic than acidic, the formula $FeO \cdot Cr_2O_3$ indicates to a chemist of to-day merely that chromite is a compound of iron, chromium and oxygen, in which the iron is bivalent and the chromium trivalent. On the other hand, the formula $Fe(CrO_2)_2$ indicates more clearly that the mineral is probably ferrous chromite.

60 to 70 per cent chromium and 1 to 8 per cent carbon. This is prepared by reducing chrome iron ore with carbon in an electric furnace. For the manufacture of chrome steel with a low percentage of carbon, it is necessary to use ferro-chrome that has been reduced by the thermite process (§ 478). (Explain why.)

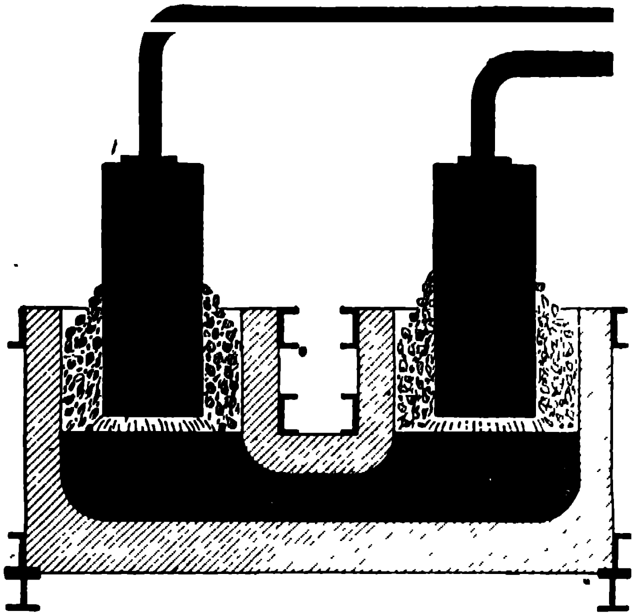

Fig. 119.—Cross-section of an electric furnace for producing ferro-chrome and other ferro-alloys. Powerful electric arcs are struck, in the midst of a charge of coke and ore, between huge graphite electrodes and a pool of molten metal.

A considerable amount of chromite ore is also converted directly into chromates by fusion with lime and sodium carbonate (§ 510).

507. Properties and Uses of Chromium.—Metallic chromium has a brilliant silvery luster, and fails to tarnish even in moist air. It is very hard, but brittle. Its chief use, in the form of ferro-chrome, is for toughening and hardening steel, but it forms hard and strong alloys with nickel, cobalt and copper. Especially interesting are the Ni-Cr alloys, **nichrome** and **illium** (§ 525), and the Co-Cr alloy, stellite (§ 520).

Chromium salts are used in tanning hides into leather, and "chrome yellow" (lead chromate) is an important yellow paint pigment (§ 554).

Chromic oxide is used as a green pigment, in coloring china-ware and porcelain. Green paints containing chromium are usually mixtures of "chrome yellow" with "Prussian blue" (§ 504).

The mineral chromite (§ 506) is sometimes molded into bricks, to be used as an intermediate neutral lining between the outer (silicious) and the inner (basic) lining of open-hearth furnaces (§ 497). Being highly infusible (m. p. above 2000° C.) and indifferent to both bases and acids, it serves very well to prevent the other two linings from reacting together to form fusible silicates.

508. Valences of Chromium. —As a metal, chromium resembles iron in forming two series of salts, in which its valence is respectively *two* and *three*:

$Cr^{II}Cl_2$ Chromous chlorid	$Cr^{III}Cl_3$ Chromic chloride
$Cr^{II}(C_2H_3O_2)_2$ Chromous acetate	$Cr^{III}(C_2H_3O_2)_3$ Chromic acetate
$Cr^{II}SO_4$ Chromous sulfate	$Cr_2^{III}(SO_4)_3$ Chromic sulfate

But chromium may enter a non-metallic radical with a valence of *six*, to form chromates or dichromates (§ 620):

$Na_2Cr^{VI}O_4$ Sodium chromate	$Na_2Cr_2^{VI}O_7$ Sodium dichromate

Corresponding to the above three valences of chromium, we know the oxides **CrO, Cr_2O_3** and **CrO_3**. Thus, the chromous and chromic salts and the chromates (or dichromates) are sometimes said to represent ***three different stages of oxidation of chromium.* Chromous salts are easily oxidized to chromic salts, and the latter to chromates or dichromates.*** **Conversely, chromates or dichromates, when reduced, give chromic salts; and, with very vigorous reducing agents, eventually chromous salts.** These changes in valence are always signalized by changes in color in the solution containing the chromium compound that is being oxidized or reduced.

Oxidation →

	2	3	6	6
Valence of Cr	Chromous salts ⇄	Chromic salts ⇄	Chromates or	dichromates
Color of solution	blue	green or violet	yellow	orange

← Reduction

509. Chromous and Chromic Salts.—1. **Chromous salts,** with chromium bivalent, may be prepared by reducing chromic salts (or a dichromate) with zinc and hydrochloric acid:

$$2CrCl_3+Zn=2CrCl_2+ZnCl_2.$$

---

* Chromates are formed in neutral or alkaline solution, and dichromates in acid solution.

Give an ionic formulation of this reaction. Give molecular and ionic formulations of the reduction of potassium dichromate to chromous chloride, by zinc in hydrochloric acid solution.

The chromous salts are **powerful reducing agents,** more active by far than the corresponding ferrous salts (§ 504).

2. **Chromic salts,** with chromium trivalent, may be prepared by reducing chromates or dichromates, with hydrogen sulfide, alcohol, or other reducing agents:

$$\underset{\text{Yellow}}{K_2CrO_4} + H_2S + HCl \rightarrow \underset{\text{Green}}{CrCl_3} + KCl + H_2O + S.$$

$$\underset{\text{Orange}}{K_2Cr_2O_7} + C_2H_5OH + HCl \rightarrow CrCl_3 + KCl + CH_3CHO + H_2O.$$

Balance these formulations (§ 135). In the second equation there is a change in the apparent valence of carbon from -2 to 0.*

Rewrite both of the balanced equations in ionic form.

Chromic salts behave in the same way as aluminum salts (§ 480), when treated with most reagents. Thus, hydrogen sulfide, in acid solution, has no action. Ammonium sulfide, ammonium hydroxide, or sodium hydroxide, precipitate chromic hydroxide, $Cr(OH)_3$, which redissolves in an excess of cold sodium hydroxide solution.

Write ionic equations, to illustrate.

Solutions of chromic salts, like those of aluminum salts, have an acid reaction, due to partial hydrolysis. This fact is applied in tanning hides into leather (§ 113). Sodium dichromate, also, is frequently used in tanning, for it is reduced to the chromic condition (Cr^{III}) by the organic matter present in the hide.

510. Preparation of Chromates and Dichromates.—**Chromates** of the alkalies are yellow crystalline salts, soluble in water. They are prepared:

1. Commercially, by heating powdered chrome iron ore with sodium hydroxide (or a mixture of sodium carbonate and lime). Oxygen is absorbed from the air.

2. In the laboratory, by oxidizing chromic hydroxide in alkaline solution (i.e., sodium chromite, Na_2CrO_2) with sodium peroxide. Sodium hydroxide and sodium chromate are produced.

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* Apparent valence, obtained by the arbitrary rule that makes hydrogen always *positive* and oxygen always *negative* (§ 120). Disregarding signs, the valence of carbon, in nearly all organic compounds, is *four* (§ 342).

Write and balance this equation. What other hydroxide, otherwise very similar to chromium hydroxide, fails to be thus oxidized?

Dichromates are formed by addition of acids to chromates:

$$2Na_2CrO_4+H_2SO_4=Na_2Cr_2O_7+Na_2SO_4+H_2O.$$

The transformation is accompanied by a striking color change, since all chromate solutions are yellow, and all dichromate solutions are orange.

Express this last statement in terms of the ionic theory.

511. Properties of Chromates and Dichromates.—1. Chromates and dichromates, in dry form, react violently with easily oxidizable substances, being reduced to *chromic oxide.*

Write and balance equations for the reduction of sodium chromate by carbon, ammonium chloride, cane sugar, metallic iron, aluminum, and red phosphorus. The sodium will appear among the reaction products as a sodium salt (sodium chromite as a last resort).

2. When concentrated sulfuric acid is added to a concentrated solution of a chromate or dichromate, beautiful dark needles of **chromium trioxide,** CrO_3, separate out:

$$K_2CrO_4+2H_2SO_4=2KHSO_4+CrO_3\downarrow+H_2O.$$

Chromium trioxide may be considered as the anhydride of the hypothetical chromic acid, H_2CrO_4. Distinguish carefully between chromic oxide, Cr_2O_3 (green powder) and chromium trioxide, CrO_3 (red needles).

3. Dichromates, in acid solution, are vigorous oxidizing agents.

Write equations for the oxidation of ethyl alcohol to acetic acid, hydrogen sulfide to sulfur and water, hydriodic acid to iodine, phosphine to phosphoric acid, and ferrous sulfate to ferric sulfate—all by means of potassium dichromate in sulfuric acid solution. Balance (§ 135).

Translate these five equations into ionic form (§ 276).

512. Tests for Chromium.—1. The presence of chromium in a solution is very frequently indicated by the **change in color** which chromium compounds undergo on oxidation or reduction. When in the **chromic condition** (valence three) chromium is usually separated, along with aluminum, by precipitation with ammonium hydroxide, and recognized by the yellow color (sodium chromate) which is developed on oxidizing the precipitate with sodium peroxide (§§ 510–2).

2. Chromium in the **chromate condition** (valence six) gives a

yellow crystalline precipitate of lead chromate, $PbCrO_4$, when the solution is tested with lead acetate.

3. If a chromate or dichromate solution is acidified with dilute sulfuric acid and shaken with a solution of hydrogen peroxide, **a blue coloration, readily soluble in ether,** is produced. This is presumed to be due to **perchromic acid,** $HCrO_4$, i.e., to chromium in a valence of seven. The blue substance is exceedingly unstable, and loses oxygen at room temperature; the color consequently disappears in a few minutes, leaving a chromic salt in solution.

MANGANESE

513. Occurrence of Manganese.—Manganese occurs in traces in most soils and in the ashes of many plants. The most important manganese mineral is pyrolusite, or manganese dioxide, MnO_2. The most important deposits of pyrolusite are in Brazil, Russia, and India. The demand for manganese for the production of steel became so great during the progress of the Great War that the United States, in a single year (1916), imported nearly half a million tons of manganese ore from Brazil alone. A great deal of **spiegeleisen** (§ 496) and manganiferous pig-iron is also smelted in the United States, directly from manganese iron ore containing from 1 per cent to 25 per cent manganese. Silver ores and zinc ores (§ 550), after being smelted, leave residues which furnish notable amounts of spiegeleisen.

514. Preparation and Properties of Metallic Manganese.—Manganese-iron ores can be reduced in a blast furnace under carefully regulated conditions, for the production of ferro-manganese and **spiegeleisen.** High-grade manganese ores are sometimes reduced by carbon in an electric furnace. To prepare the pure metal, free from carbon, it is necessary to resort to the thermite process, as in the case of chromium (§§ 478, 506).

Pure manganese is a hard but brittle metal, which resembles iron very closely in its general appearance. It is much more readily oxidized than iron, however, and decidedly more active chemically, as is indicated by its position in the electro-chemical series (§ 422).

515. Uses of Manganese.—(1) Most of the manganese ore mined is used in the **steel industry.** (2) A very large quantity of manganese dioxide is now used in the manufacture of **dry cells,** as a depolarizer (§ 423). (3) Manganese forms many useful alloys with copper and nickel. **Manganin** wire is used for electrical resistance-coils. Though it contains about 80 per cent copper (10 per cent Ni, 10 per cent Mn), its resistance is nearly thirty times that of pure copper, and is very much more nearly constant with changing temperature.

516. Valences of Manganese.—Review § 508. Manganese shows an even greater versatility than chromium in changing valence in the presence of oxidizing and reducing agents. Compounds are known in which the element has the valences two, three, four, five, six and seven. But **whereas with *chromium* the stable and important compounds are those in which the metal has the valences three and six, with *manganese* the most noteworthy valences are two and seven.**

Compare the formulas:

$Cr^{II}Cl_2$ Chromous chloride	$Cr^{III}Cl_3$ Chromic chloride	$Na_2Cr^{VI}O_4$ Sodium chromate	$HCr^{VII}O_4$ Perchromic acid (unstable)
$Mn^{II}Cl_2$ Manganous chloride	$Mn^{III}Cl_3$ Manganic chloride (unstable)	$Na_2Mn^{VI}O_4$ Sodium manganate	$HMn^{VII}O_4$ Permanganic acid

Here again, the changes in valence are marked by striking changes in color:

Oxidation
$\longrightarrow$

	2		6		7
Valence of Mn	Manganous salts	$\rightleftarrows$	Manganates	$\rightleftarrows$	Permanganates
Color of Solution	pink (or colorless)		green		purple

$\longleftarrow$
Reduction

517. Manganates and Permanganates.—**Manganates** are prepared by fusing manganese dioxide with oxidizing agents, in the presence of alkali:

$$KOH + MnO_2 + KClO_3 \rightarrow \underset{\text{Potassium manganate}}{K_2MnO_4} + H_2O + KCl.$$

Balance this equation.

Manganates are stable only in the presence of alkali. If an acid is added, even so inactive a one as carbonic acid, the color of the solution changes from green to purple, owing to the formation of a permanganate, and a brown precipitate of hydrated manganese dioxide appears:

$$\underset{\substack{\text{Potassium}\\\text{manganate}\\\text{(green)}}}{\mathrm{3K_2MnO_4}}+\mathrm{2H_2CO_3} \rightarrow \underset{\substack{\text{potassium}\\\text{Permanganate}\\\text{(purple)}}}{\mathrm{2KMnO_4}}+\mathrm{MnO_2}+\mathrm{2K_2CO_3}+\mathrm{2H_2O}.$$

Or, the reaction may be explained by assuming that the potassium manganate is hydrolyzed, and that the product, $\mathrm{H_2MnO_4}$, then decomposes.

Give molecular and ionic formulations of the hydrolysis.

Permanganates are important *oxidizing agents*. In acid solution they are reduced to manganous salts; in neutral or alkaline solution, to $\mathrm{MnO_2}$:

$$\mathrm{KMnO_4+FeSO_4+H_2SO_4 \rightarrow Fe_2(SO_4)_3+K_2SO_4+MnSO_4+H_2O};$$

$$\mathrm{KMnO_4+C_2H_5OH \rightarrow KC_2H_3O_2+KOH+MnO_2+H_2O}.$$

Balance these two equations.

Rewrite them in ionic form, and explain the first as a transfer of electrons.

If we were oxidizing ferrous sulfate in dilute solution, how could we tell when enough potassium permanganate solution had been added?

What weight of potassium permanganate must be taken to prepare a liter of N/10 solution (§ 175), which is to be used for oxidation purposes in the presence of an acid, and in presence of a base, respectively?

518. Tests for Manganese.—(1) When a trace of a manganese compound is fused on a platinum foil with sodium carbonate and a little potassium nitrate, a green color is developed.

To what is this color due?

If manganous sulfate were the substance tested, what would become of the sulfate radical during fusion? What gaseous product would be formed? Write and balance equation.

(2) When a manganese compound is boiled with dilute nitric acid, in the presence of powdered lead dioxide, it is oxidized by the latter to permanganic acid. This imparts a purple color to the solution as soon as excess of lead dioxide has settled out. The test is an exceedingly delicate one:

$$Mn(NO_3)_2+HNO_3+PbO_2 \rightarrow \underset{\text{Purple}}{HMnO_4}+Pb(NO_3)_2+H_2O.$$

Balance this equation.

Halides must be absent. Why? How can they be removed if present?

Lead dioxide sometimes contains manganese dioxide as an impurity. How could this be detected?

A very similar reaction takes place when sodium bismuthate,* or ammonium persulfate, $(NH_4)_2S_2O_8$, with a little silver nitrate as catalyzer, is added to a solution of a manganous salt in nitric acid. The reaction with sodium bismuthate takes place in the cold, and in a boiling solution MnO_2 is precipitated. With persulfate, the reaction is best accomplished in a warmer solution, and MnO_2 is precipitated unless the catalyzer is present.

Balance the equation:

$$Mn(NO_3)_2+(NH_4)_2S_2O_8+H_2O \rightarrow HMnO_4+(NH_4)_2SO_4+H_2SO_4+HNO_3.$$

EXERCISES.

1. Write equations for the reduction of chromite and pyrolusite by the thermite process.
2. Write and balance equations for the action of potassium dichromate and potassium permanganate on concentrated hydrochloric acid.
3. Give an ionic equation for the reduction of chromic chloride to chromous chloride by metallic zinc, in hydrochloric acid solution. Explain as a transfer of electrons.
4. Write equation for the preparation of potassium dichromate from potassium chromate, in the presence of hydrochloric acid. Express this in ionic form.
5. What happens when a solution of sodium chromate is treated with each of the following: dilute sulfuric acid, hydrogen sulfide, barium chloride, lead acetate? Express by ionic equations.
6. How may sodium manganate be prepared from manganese dioxide? What is the color of this salt? Under what conditions is it stable? How may it be transformed into sodium permanganate?
7. Write equations for the oxidation of hydrogen sulfide, ferrous sulfate, oxalic acid (to carbon dioxide) and nitrous acid (to nitric acid) by potassium permanganate in acid solution. Balance. Which element is oxidized and which reduced in each case?
8. Write an equation for the oxidation of chromic hydroxide to sodium chromate by sodium peroxide, the other product being sodium hydroxide. Balance.
9. Write and balance equation for the decomposition of ammonium dichromate by heat, the products being chromic oxide, water, and nitrogen. What weight of ammonium dichromate is needed to prepare 44.8 cc. of nitrogen at standard conditions?

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* The material called sodium bismuthate is really a mixture containing Na_2O and BiO_2 in variable proportions.

CHAPTER XL

COBALT AND NICKEL

519. General Properties of Nickel and Cobalt.—1. Cobalt and nickel resemble iron in being much more **magnetic** than other elements. Indeed, an alloy of cobalt and copper may be magnetized as intensely as iron itself.

2. Cobalt and nickel, unlike iron, are **not rusted in moist air,** and oxidize only at high temperatures.

3. The order of the metals of the iron family in the electrochemical series is Mn, Fe, Co, Ni. Thus, **cobalt and nickel are less readily dissolved by acids than is iron,** and alloys of cobalt and nickel with other metals are more resistant still.

4. The atomic numbers of the metals of the iron family place them in the same order in the periodic system as in the electrochemical series.* Indeed, **the chemical properties of cobalt are roughly intermediate between those of iron and nickel.** Cobalt, like iron, forms a number of salts in which it has a valence of three, while nickel does not.

Order of decreasing stability

→

Ferric salts	*Cobaltic salts*	*Nickelic salts*
stable	unstable	non-existent

The ordinary valence of cobalt and nickel is, however, two.

COBALT

520. Metallic Cobalt and Its Alloys.—Cobalt is found as an arsenide or sulfide, in association with nickel and other metals. From such ores, nickel and cobalt are separated together by a roasting and reduction process presently to be described (§ 523).

Metallic cobalt is a bright silvery metal with a slight bluish cast. It is not easily oxidized or tarnished, or corroded by acids, but is less abundant than nickel, its nearest rival, and is somewhat less brilliant. The most important cobalt alloy is **stellite** (Co, 75 per cent; Cr, 16.5 per cent; small amounts of W or Mo, Ni, Fe, C, Si). This is not only very resistant toward acids, but is hard and tough enough to hold a cutting edge. It is used for cutlery and surgical instruments; and even for lathe tools, in competition with tungsten steel (§ 501).

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* This is one of the three instances in which the order of atomic weights is not the same as the order of atomic numbers.

521. Compounds of Cobalt.—A blue glass, known as **smalt**, is made by fusing sand with potassium carbonate and a little cobalt oxide. This has been used since ancient times for coloring ceramic products. Another blue pigment, cobalt aluminate, has already been mentioned as the product of an analytical test for aluminum.

Cobalt chloride, $CoCl_2 \cdot 6H_2O$, crystallizes in red prisms, which turn blue when dehydrated by heating. This is the secret of the so-called sympathetic inks.

A mixture of the oxides of cobalt, copper, manganese, and sometimes silver, known as **hopcalite,** is used in gas masks as a catalytic agent to bring about the oxidation of carbon monoxide. This gas is not appreciably removed by ordinary absorbents (activated charcoal and silica jelly).

Salts with cobalt in a valence of three are not very stable, unless cobalt enters into a complex ion (§ 536). An example of such a substance is potassium cobalticyanide, $K_3Co(CN)_6$, analogous to potassium ferricyanide. Chemists are interested in the fact that cobalt (and, to a less extent, nickel) form many complex compounds with ammonia and cyanogen. These furnish the best-known inorganic illustrations of **isomerism**—the existence of compounds with identical empirical formulas, but differing in chemical properties because of differences in the arrangement of the atoms within their molecules (§ 342).

522. Analytical Tests for Cobalt.—In analytical chemistry, cobalt is detected by the blue color that it imparts to the borax bead (cobalt metaborate, $Co(BO_2)_2$), and by the yellow precipitate (potassium cobaltinitrite, $K_3Co(NO_2)_6$) that it gives with potassium nitrite in acetic acid solution. Cobalt salts also give a precipitate with β-nitrosophenol. Otherwise, the reactions of cobalt are very similar to those of nickel and ferrous iron.

NICKEL

523. Occurrence and Metallurgy of Nickel.—Most of the nickel now produced comes from the Sudbury district, Ontario, Canada, where it occurs as a sulfide associated or combined with copper sulfide and iron sulfide. Minor deposits of nickel ores are found in New Caledonia, Norway, and Germany. The world now produces about 40,000 tons of nickel (pure or in the form of alloys) each year. About a thousand tons of this comes from the United States, where it is obtained as a by-product of the electrolytic refining of copper (§ 531).

The metallurgy of nickel is extremely complicated. The process begins with the roasting, or partial oxidation of the sulfide ores, by a blast or air in the presence of silica in a Bessemer converter. This removes much of the iron as iron silicate (details in § 530). The result is a purified copper-nickel sulfide, or **matte.**

In the Canadian process, the matte is mixed with sodium sulfate and partially reduced with carbon in a small blast furnace:

$$Na_2SO_4+C \rightarrow Na_2S+CO\uparrow .$$

The molten product is drawn off into ladles, in which it forms two layers, the lower one largely NiS, the upper one largely a solution of CuS in Na_2S. When the material has solidified, the two layers are separated, and the lower layer roasted and reduced with coke, above the melting-point of nickel (1450° C.). The molten metal tapped from the furnace is cast into anodes for electrolytic refining or deoxidized with manganese or magnesium to produce malleable nickel.

524. Properties and Uses of Metallic Nickel.—Metallic nickel is extremely hard, brilliant, and resistant to the action of the atmosphere and acids. For this reason other metals are frequently protected by **nickel-plating.** The process is similar to that described for copper in § 533.

Ordinary nickel cannot be rolled or drawn into wire, on account of the presence of small amounts of oxide, which tend to render it brittle; but if it is deoxidized just previous to casting, by the addition of a few per cent of metallic magnesium or manganese, it becomes malleable and ductile. In the laboratory, nickel crucibles are often used for fusing chromite and other minerals with the caustic alkalies. Platinum would be ruined by such uses.

Other important uses for metallic nickel are as a catalyzer in the hydrogenation of oils (§ 76); as spark terminals in ignition systems (in competition with tungsten); and in radio-amplifiers. Nickel and nickel oxide are used in the Edison storage cell; and nickel oxide is a constituent of the "under-body," or first coating, in enameling steel.

525. Nickel Alloys.—No other metal forms so great a number of useful alloys as nickel. These are as brilliant in luster as nickel itself, even more resistant to corrosion, and have high melting-points, high electrical resistance, and other valuable properties.

The nickel alloys fall into five groups:

1. **Nickel Steel.**—About 60 per cent of all the nickel now produced goes into nickel steel. We have already mentioned the extraordinary resistance of this material to corrosion, and the fact that its rate of expansion with changing temperature (invar, § 501) is extremely slight.

2. **Acid-resisting Alloys.**—The most important of these is **monel** (Ni, 67 per cent; Cu, 28 per cent; small amounts of Fe, Mn). This is used for dipping baskets, to contain small castings to be pickled in acid, preparatory to nickel plating, for acid pumps, etc. The high-pressure steam pipes on many American warships are fitted with monel-metal valves. In the chemical industries, cloth woven of monel wire is sometimes used in filter presses for filtering acid liquors. Monel-metal fly screens, for doors and windows, may be left exposed to the weather the year around, without corroding.

With a much lower percentage of nickel (10 per cent to 40 per cent) we have a series of cupro-nickel alloys which are quite resistant to corrosion, and, when deoxidized with magnesium or copper-manganese alloy, are extraordinarily malleable and ductile. Such an alloy is used for condenser tubes and feed-water heaters on the vessels of the United States Navy, and for bullet jackets in small-arms ammunition.

Another important alloy of this class is **illium** (Ni, 61 per cent; Cr, 21 per cent; Cu, 6 per cent; Mo, 5 per cent; small quantities of Fe, Al, W, Si Mn). This may be turned in a lathe. It is used for calorimeter bombs (§ 332), a situation in which a metal is exposed to the destructive action of compressed oxygen at a high temperature.

Still another very promising acid-resisting alloy contains nickel, with 10 per cent to 18 per cent tungsten. This is sufficiently malleable to be rolled into sheets.

3. **Electrical Resistance Alloys.**— Many alloys of nickel with chromium, copper, iron, or manganese have a very high electrical resistance—in an extreme case as much as seventy times the resistance of copper. These are of great industrial importance, at the present time, for the manufacture of household conveniences, such as electric stoves, toasters, and flat irons; and for wiring small electric furnaces and rheostats.

Nichrome will stand long heating at temperatures around 1000° C., without appreciable oxidation. It has been used for boxes for case-hardening (§ 500) or annealing. Another use is in machinery for melting and working glass—a good example of how progress in one chemical industry usually works out to the immediate advantage of others.

Manganin and **constantan** are valued because of the constancy of their electrical resistance with varying temperature.

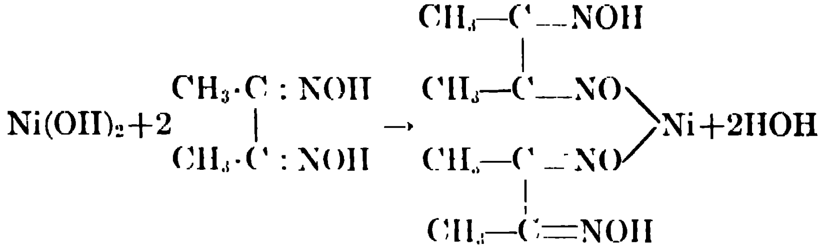
	Approx. Ratio of Res. (0° C.) to Res. of Cu	Percentage Composition.				
		Ni	Cr	Cu	Mn	Fe
Nichrome	70	60	12	. .	2	26
Chromel A	64	80	20			
Nickelene	20	15	. .	60	(Zn = 25)	
Constantan.	31	40 to 55	.	45 to 60		
Manganin .	28	2 to 16		50 to 85	10	

4. **Nickel Alloys Related to Brass and Bronze.**– The addition of a small amount of nickel to brass or bronze gives the material added toughness, somewhat increased resistance to corrosion, and other valuable properties. *Nickelene,* or *nickel silver* (formerly called German silver), which is used for electrical resistance wire, for service at moderate temperatures, has very nearly the color of silver, and is very much used as a base metal in articles to be silver plated.

5. **Coinage and Jewelry.**—A very small amount of nickel will deprive copper or gold of its color, and that in spite of the fact that no chemical compound is produced between the metals in either case. The American 5-cent piece contains about 75 per cent copper and only 25 per cent nickel. White gold, an alloy of 20 to 50 per cent nickel, and the rest gold, is used in imitation of platinum, in jewelry.

526. Analytical Tests for Nickel.—Nickel salts, when fused with borax, give a brown bead.

Another special test consists in the addition of **dimethyl glyoxime** to a solution of nickel salt made very faintly alkaline with ammonium hydroxide. A beautiful **strawberry-red precipitate** is produced—**the acid nickel salt of dimethyl glyoxime.**



$$Ni(OH)_2+2\begin{array}{c}CH_3\cdot C:NOH\\ |\\ CH_3\cdot C:NOH\end{array}\rightarrow \left.\begin{array}{l}CH_3-C-NOH\\ \qquad |\\ CH_3-C-NO\\ CH_3-C-NO\\ \qquad |\\ CH_3-C=NOH\end{array}\right\rangle Ni+2HOH$$

EXERCISES

1. List the oxides corresponding to the different standard valences of the five elements of the iron family. Which of these oxides have base-forming and which acid-forming properties?

2. A solution obtained by extracting a roasted ore with acid contains sulfates of both nickel and copper. What would be the effect, if any, of trickling this solution over scrap nickel? Scrap copper? State the principle involved.

3. A solution containing both nickel and copper sulfates is electrolyzed, the electromotive force being slowly raised. Which metal will be deposited first? State the principle involved.

4. State the chief differences in the chemical behavior of the elements nickel and cobalt.

5. Give equations showing the formation of potassium cobaltinitrite from cobalt chloride and potassium nitrite in acetic acid solution. Nitrous acid is liberated, which oxidizes the cobalt to the cobaltic condition, and is itself reduced to nitric oxide.

6. Rewrite the preceding equations in ionic form.

7. What are the following: invar, stellite, illium, constantan, nichrome?

CHAPTER XLI

COPPER

Since we began the study of the metals, several chapters back, we have been working from left to right across the periodic table, selecting only the most important elements: first the alkali metals, then the alkaline earth metals, then aluminum, then iron. The electropositive character of these elements decreases in the order given, though all of them are a considerable distance above hydrogen in the electrochemical replacement series. But, after passing through the transition group (containing iron) we meet copper, silver, and gold—a group of metals very strikingly different from any we have yet discussed.

527. Characteristics of Copper, Silver, and Gold.—The following table will emphasize this contrast:

Na, Ca, Al, Fe, etc.	*Cu, Ag, Au*
Never found native (except Fe, rarely).	Often found native.
Easily rusted or corroded (except Cr, Ni, Co) when exposed to moist air.	Not subject to rust, nor easily corroded.
Displace hydrogen from water and dilute non-oxidizing acids.	Have no effect on water or dilute non-oxidizing acids.
Form stable oxides, not decomposed by heating.	Oxides of silver and gold easily decomposed by heat.
Sulfides not precipitated by hydrogen sulfide in acid solution.	Sulfides precipitated by hydrogen sulfide in acid solution.
Halides all soluble in water.	Halides (in valence one) insoluble.

528. The World's Copper Resources.—The most important copper ores are: (1) Native copper. (2) Complex oxides and sulfides of copper, in association with other metals—chiefly iron, nickel, lead, silver, gold. (3) Silicates and basic carbonates of copper (including decorative stones like malachite and azurite).

The United States has produced as much as a million tons of copper a year, and regularly furnishes about two-thirds of the world's output. Indeed, the six leading copper-producing states (Arizona, Montana, Utah, Nevada, Colorado, and Michigan) outrank the six leading foreign countries (Mexico, Spain, Japan, Cuba, Australia, and Chile).

This predominance of the United States is not due to any monopoly of copper ore—for every continent has enormous deposits—but largely, as in the case of the iron and steel industry, to local conditions that have combined to favor the development of production on a stupendous scale. The one city of Butte, Montana, has a copper-smelting capacity equal to the combined production of any two foreign countries.

529. Froth Flotation.—One of the most interesting of recent advances in the metallurgical art has been the development of the **froth-flotation process** for concentrating ores. This is an application of the familiar fact that liquids will wet certain substances but not others. Water, for example, will wet glass, but not paraffin.

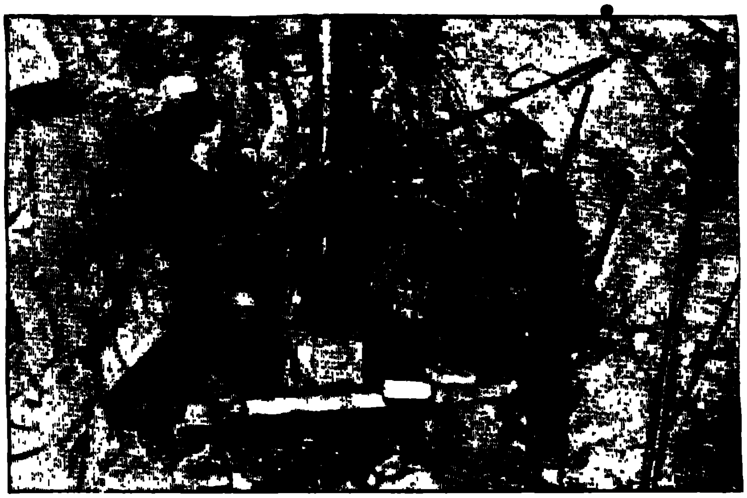


FIG. 120—Mining copper ore with an air drill.

A little pine oil or mineral oil is mixed with the finely ground ore suspended in water. Air is then bubbled through the suspension, and rises to the surface as a froth or foam—innumerable individual bubbles of gas, each surrounded by a film of oil. Now it happens that the valuable constituents of copper ore (mainly copper sulfide or metallic copper) are more easily wet by the oil than the silicious part, or gangue. The gangue settles to the bottom, but the ore particles are drawn into the film of oil surrounding the rising air bubbles or into the surface separating oil from water. Each bubble is thus, in effect, **armor-plated** by a layer of ore particles, and the stability of the froth or foam is very much increased. If the process is carried out with care, as much as 90 per cent of the copper in the ore will be found in the froth; and the material to be treated in the subsequent smelting process may be reduced to a fifteenth of its original bulk.

The froth-flotation process is now conducted on an enormous scale for the concentration of low-grade ores of a number of different metals. Of copper ore alone, in the United States, it is estimated that not less than 60 million tons are now treated annually (1920). Ores that could not be worked profitably under the older methods of concentration are now mined and smelted. Vast deposits of minerals in all parts of the world have been made available to civilization, and our known reserves of useful metal, in a single stroke, have been extended more than is usually accomplished by a generation of prospecting and exploration.

530. Copper Smelting.— The concentrates from the froth-flotation process consist as a rule of cuprous sulfide (Cu_2S) and chalcopyrite ($CuFeS_2$) in association with sulfides of lead, arsenic, and other elements, and a certain amount of silicious material. The treatment of these concentrates varies with their composition, and may be quite complex. *Roasting to remove sulfur, followed* by reduction by coke in a blast furnace, would hardly serve, because the iron, lead, and other metals accompanying the copper would also be reduced.

With carbonate and oxide ores, a **wet method** has sometimes been used – extraction with sulfuric acid, followed by precipitation of the copper by metallic iron. But at the present time most of the copper produced is obtained by a dry method of smelting, carried out in two stages:

(1) The froth-flotation concentrates are dried, mixed with a silicious flux, and melted in a reverberatory furnace of the same general design as the puddling furnace for making wrought iron (§ 494). The sulfides are partially oxidized, and the copper separates as an easily fusible, impure cuprous and ferrous sulfide, known as **copper matte.** A large part of the iron is slagged away as ferrous silicate:

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2,$$
$$2FeS + 3O_2 = 2FeO + 2SO_2.$$
$$FeO + SiO_2 = FeSiO_3.$$

(2) The fused matte is tapped from the reverberatory furnace, separated from the overlying layer of liquid slag, and transferred to a copper converter, much like that used in the manufacture of Bessemer steel (§ 496). A blast of air is then blown through the charge, oxidizing the lead and iron sulfides to the corresponding metallic oxides, which form a silicate slag by uniting with a silicious flux, added for that purpose.

Certain amounts of cuprous and cupric oxides are formed at the same time, but these are reduced by the unchanged cuprous sulfide to form metallic copper:

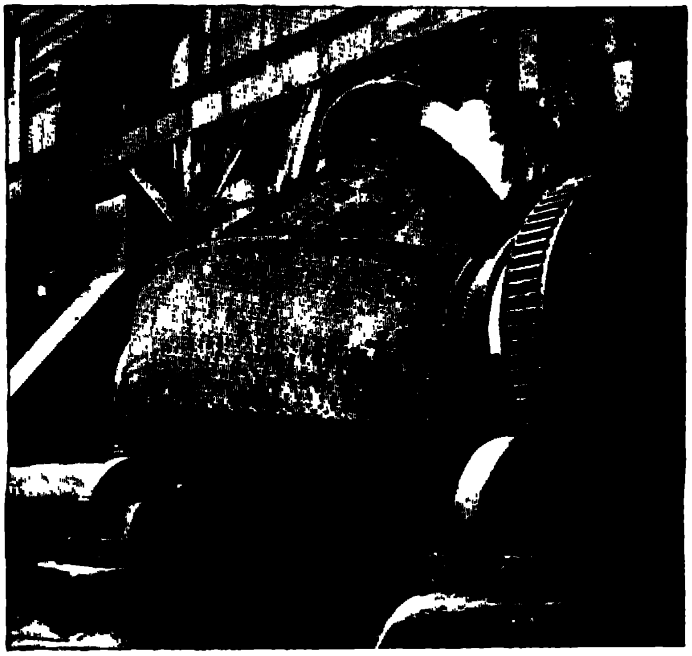


FIG 121 —A copper converter in action. This one stands over 20 ft. high. Notice the massive trunnions and gears, for tilting the converter, to pour out the finished copper. The supports must be solidly built, for the converter is constructed of heavy steel plates, lined with magnesia brick, and with its charge of matte weighs 300 tons. A 100 horse-power electric motor supplies power for tilting.

$$2CuO + Cu_2S = 4Cu + SO_2.$$

The product of the copper converter is known as **blister copper,** on account of the blisters, or bubbles, formed by the escape of SO_2 during solidification. It is further purified, by gentle oxidation in a refining furnace, then cast into anodes for electrolytic refining. Blister copper contains 2 or 3 per cent of impurities, which make it useless for applications requiring mechanical strength or high electrical conductivity.

531. The Electrolytic Refining of Copper.—Review §§ 422, 424. Almost all the copper used in industry is refined (purified) by electrolysis. Heavy plates of impure copper form the anodes. The cathodes are thin sheets of pure copper; and the electrolyte is a solution of copper sulfate in sulfuric acid.

The gold and silver contained as impurities in the anode fail to dissolve; for these metals are much below copper in the electrochemical series (§ 424). They accordingly subside as a fine sludge (anode mud) which is recovered when the electrolyte is drained from the electrolytic cell. Iron, zinc, and lead, on the other hand, are brought into solution along with the copper; but they fail to be deposited upon the cathode, for they are above copper in the electrochemical series, and have the additional handicap of being present only in small concentrations. The same is true of hydrogen, which fails to be evolved in any considerable amount, even though the electrolyte may be strongly acid with sulfuric acid.

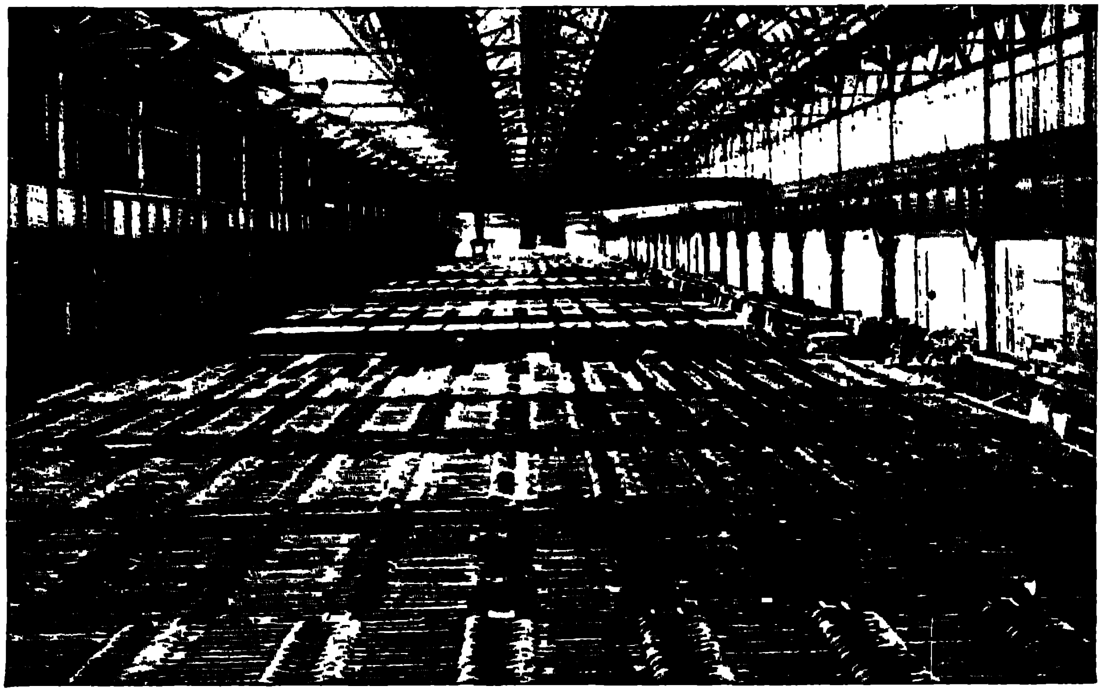


FIG. 122.—An electrolytic copper refinery. This building contains 1800 tanks, each with 28 anodes and 29 cathodes arranged alternately A traveling crane, in the middle distance, handles the 500-lb. anodes of blister copper, and the 135-lb. finished cathodes of refined copper.

Copper is thus continuously dissolved from the anode and redeposited on the cathode. The impurities contained in the anode are removed by something like a double sifting process, gold and silver being got rid of as anode mud, while the more soluble impurities remain in solution, as the copper comes out upon the cathode.

532. Properties and Uses of Metallic Copper and Its Alloys.—Pure copper and many of its alloys are remarkably tough and strong, but they are at best inferior to mild steel in tensile strength and to high-carbon steel in hardness. They are therefore applied to uses that put a premium on the qualities in which copper is superior to iron and steel: *ductility, malleability, resistance to corrosion,* and *high electrical conductivity.*

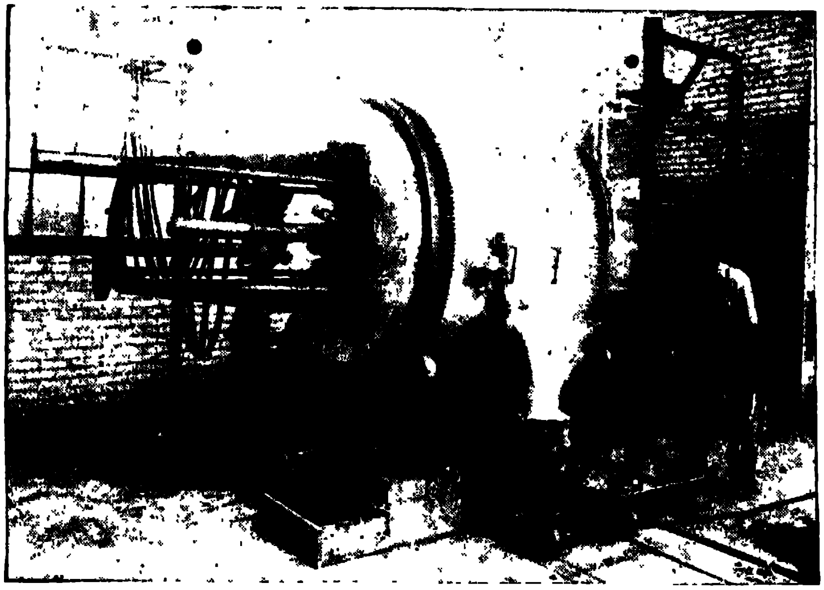


FIG. 123 —An electric furnace for melting brass. In a furnace of this type the temperature can be controlled very accurately, and metals melted without access of air.

Large amounts of pure electrolytic copper are used for roofing; for covering ships' bottoms; for linings and tubing in kettles, evaporators, and condensers; and in the electrical industries. **Bronze** is a copper alloy containing 3 to 8 per cent of tin, and 11 per cent or more of zinc. It is much harder than pure copper; and is a substitute for steel in castings requiring mechanical strength, but in which even a small amount of rusting would be objectionable (laundry machinery, propeller blades, paper pulp beaters). Large quantities are used in coins and statuary.

Brass contains 18 per cent to 40 per cent zinc. It is inferior to pure copper in strength and pliability, but melts at a lower temperature, is easily cast and machined, and is not subject to rusting. But in contact with metals below it in the electrochemical replacement series it is readily attacked, the zinc disappearing in a very short time, leaving a brittle spongy mass of copper behind. Alloys of copper with aluminum (§ 477) and nickel (§ 525) are described elsewhere.

533. Electrotyping.—Copper may be deposited electrolytically in tough, smooth films of extreme thinness. This property is applied in the **electrotyping process.** Type is first set up for a page of a book, and an impression is made in wax. This wax is covered over with finely powdered graphite, to give it a conducting surface, then made cathode in a copper sulfate solution containing a trace of gelatin or glue. A heavy plate of copper serves as anode. When the deposit of copper on the graphited surface has been built up to about the thickness of a sheet of paper, it is stripped away and strengthened by filling in the back with melted lead. Text-books are commonly printed from such copper plates or electrotypes. These wear longer than zinc etchings, and call for a smaller investment of capital than would be needed were the original type metal held over for a period of several years between successive printings.

534. Chemical Characteristics of Copper.—Some of the chief chemical characteristics of copper are indicated by its position in the periodic table:

1. Copper is a typical heavy metal. Solutions of its salts accordingly react acid, owing to slight hydrolysis.

2. Its characteristic valences are one (cuprous salts) and two (cupric salts). **Most *cuprous* salts are colorless, and most *cupric* salts are blue or green.**

3. Like most other heavy metals, copper forms insoluble oxides, hydroxides, carbonates, phosphates, and oxalates (§ 426).

4. When copper salts of organic acids or of acids having volatile anhydrides are ignited in the air, cupric oxide is left behind:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2,$$
$$Cu(C_2H_3O_2)_2 + 4O_2 = CuO + 4CO_2 + 3H_2O.$$

5. **Metallic copper is dissolved only in traces by dilute non-oxidizing acids, in the absence of air. But in the presence of air, and especially of air and a cupric salt, it may be dissolved very rapidly.** The explanation is that solutions of cupric salts oxidize metallic copper, and are reduced by it to the cuprous condition:

$$Cu + CuCl_2 = 2CuCl.$$

The cuprous salt thus formed is reoxidized to the cupric condition by the oxygen of the air, and is then able to dissolve a fresh portion of metal:

$$4CuCl+4HCl+O_2=4CuCl_2+2H_2O.$$

Corrosion of sheet copper by a dilute acid in the presence of air, when once begun, thus goes on with increasing rapidity.

Ionically the dissolving of copper by an acid solution of a cupric salt and the reoxidation of the product would be formulated:

$$Cu+Cu^{++}=2Cu^+,$$
$$4Cu^++4H^++O_2=4Cu^{++}+2H_2O.$$

The process in the end thus consists in the transfer of electrons from copper atoms to hydrogen ions. This, of course, results in a decrease in the total acidity (H^+-concentration) in exact proportion to the amount of copper dissolved.

6. **Metallic copper is precipitated from solutions of its salts by iron, zinc, lead, and most of the other heavy metals** (as is indicated by its position in the electrochemical series).

535. Why Precipitated Copper Compounds are Soluble in Ammonium Hydroxide.—When an excess of ammonium hydroxide is added to precipitated copper hydroxide, the latter dissolves, forming an intensely dark-blue solution, sometimes used as a solvent for cellulose in preparing artificial silk (§ 370). This effect is presumed to be due to the fact that ammonium hydroxide molecules dissociate to form molecules of ammonia, which then combine with some of the cupric ions in solution, to form **complex cupric-ammonia cations,** $Cu(NH_3)_4{}^{++}$. These are responsible for the dark-blue color.

$$\begin{tikzcd}
\underset{\text{Precipitated}}{Cu(OH)_2} \arrow[r, shift left, "(1)"] & \underset{\text{Dissolved}}{Cu(OH)_2} \arrow[l, shift left, "(4)"] \arrow[r, shift left, "(2)"] & Cu^{++} \arrow[l, shift left, "(3)"] & +2OH^-, \\
 & & + & \\
 & 4NH_4OH \arrow[r, shift left] & 4NH_3 \arrow[l, shift left] \arrow[d, shift left, "(5)"] & 4H_2O \\
 & & \underset{\substack{\text{Complex}\\ \text{cation}}}{Cu(NH_3)_4{}^{++}} \arrow[u, shift left, "(6)"] &
\end{tikzcd}$$

But the withdrawal of Cu^{++} ions in this way (reaction 5) from a solution in equilibrium with precipitated $Cu(OH)_2$ must plainly favor the reactions from left to right (1 and 2) and perhaps result in all the precipitate being dissolved. The same result would, of course, be obtained if the precipitated substance, instead of being

$Cu(OH)_2$, were a slightly soluble cupric salt, capable of furnishing Cu^{++} ions to the solution.

Accordingly, **all slightly soluble cupric salts, except CuS, are redissolved by an excess of ammonium hydroxide, the increased solubility being due to the withdrawal of Cu^{++} ions from solution, by combination with NH_3, to form complex cupric-ammonia ions, of the formula $Cu(NH_3)_4{}^{++}$.** Cupric sulfide fails to be redissolved because of its extreme insolubility. So very little of this substance dissolves in pure water that its solubility may be increased several hundred fold by the addition of ammonium hydroxide, and still remain imperceptible.

536. Some Other Complex Copper Ions.—Copper salts furnish a number of other cases of increased solubility due to the presence of complex ions. Cuprous chloride, CuCl, is a white powder, insoluble in water, but easily brought into solution by ammonium hydroxide. The common explanation is that cuprous ions unite with NH_3 to form complex cupro-ammonia ions, $Cu(NH_3)_2{}^{+}$. Cuprous chloride is also soluble in hydrochloric acid, and cuprous cyanide in potassium cyanide solution:

$$CuCl + HCl = HCuCl_2;$$
$$CuCN + KCN = KCu(CN)_2.$$

The two compounds here formed are not double salts (§ 447) but **complex salts,** having copper in the non-metallic radical. Otherwise expressed, they furnish **complex anions,** $(CuCl_2)^-$ and $[Cu(CN)_2]^-$.

Ionically formulated, the dissolving of CuCl in HCl would appear:

$$\begin{array}{lcl} \underset{\text{(Solid)}}{CuCl} \rightleftarrows CuCl \rightleftarrows & Cu^+ & + Cl^-, \\ & + & \\ HCl \rightleftarrows & H^+ & + Cl^- \\ & & \quad \upharpoonleft\!\downharpoonright \\ & & (CuCl_2)^- \end{array}$$

and similarly for the dissolving of CuCN in KCN. The presence of copper in a negatively charged ion is of course exactly contrary to the usual behavior of metals; but it seems to be confirmed by the fact that when an electric current is passed through a solution containing the assumed complex salt, $K \cdot Cu(CN)_2$, the movement of copper through the solution is for the most part toward the *anode.* There nevertheless remain enough Cu^+ ions present to furnish a deposit of copper on the *cathode,* in exact accordance with Faraday's law (§ 425).

537. Analytical Tests for Copper.—Cuprous salts are quickly oxidized to the cupric condition on exposure to air. The **common analytical tests for copper** are, therefore, those for the metal in its higher valence:

1. **Ammonium hydroxide** in excess develops a deep blue color, ascribed to the complex ion, $Cu(NH_3)_4^{++}$ (§ 535). This is a much more intense blue than that shown by the same concentration of copper in the absence of ammonia. The test will detect copper in a concentration of about one part in a million.

2. **Potassium ferrocyanide, $K_4Fe(CN)_6$**, develops a dark red color, due to **cupric ferrocyanide, $Cu_2Fe(CN)_6$**. This test, in neutral or faintly acid solution, is several times as sensitive as the previous one.

3. When **potassium iodide** is added to a solution of a cupric salt, the resulting cupric iodide decomposes at once, forming **cuprous iodide and iodine:**

$$CuSO_4+2KI=CuI_2+K_2SO_4,$$
$$2CuI_2=2CuI+I_2.$$

The quantity of iodine thus liberated may be determined by titration with sodium thiosulfate (§ 237), and the copper in the original solution thus estimated indirectly; for each gram atom of free iodine is derived from one gram-molecule of cupric iodide, and thus corresponds to one gram-atom of copper.

4. When **potassium cyanide** is added to a solution of a cupric salt, cuprous cyanide is precipitated, and free cyanogen evolved:

$$CuSO_4+2KCN=Cu(CN)_2+K_2SO_4,$$
$$2Cu(CN)_2=2CuCN\downarrow+(CN)_2\uparrow.^*$$

The reaction is very similar to that just given for cupric sulfate and potassium iodide. But in this case the precipitate redissolves in an excess of the precipitating reagent, forming a **colorless solution of potassium cupro-cyanide:**

$$CuCN+KCN=KCu(CN)_2.$$

538. Some Important Compounds of Copper.—1. **Cupric sulfate** is made by action of dilute sulfuric acid on copper in presence of air; or by oxidizing cuprous sulfide in a furnace and dissolving the mixed cupric oxide and sulfate in dilute sulfuric acid. It is used in copper plating (§ 533); as a mordant in dyeing (§ 372); and in traces in drinking water to discourage the growth of microscopic plants (algae) that sometimes give to the water a disagreeable odor and taste. When cupric sulfate solution is mixed with lime water, a suspension of calcium sulfate and cupric hydroxide is formed (**Bordeaux mixture**). This is used as a spray to combat fungi on plants. The wine industry of Southern France, and the coffee industry of Java have in the past been saved from destruction by the use of this remedy.

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* This reaction is often used to decolorize a blue ammoniacal solution of a cupric salt. In that case there is no precipitation of CuCN, and no $(CN)_2$ is evolved, but NH_4CNO is formed.

2. **Cupric chloride,** in hydrochloric acid solution, is reduced to cuprous chloride by boiling with metallic copper or by stannous chloride or sulfurous acid.

3. **Cuprous chloride,** a white powder insoluble in water, is soluble in ammonium hydroxide or in concentrated hydrochloric acid, presumably on account of the formation of complex ions (§ 536). Such solutions are used in gas analysis as solvents for oxygen and carbon monoxide (§ 280).

4. **Cupric hydroxide** dissolves in ammonium hydroxide (§ 535) and in solutions of many organic substances, for example, sodium potassium tartrate (Fehling's solution, § 366).

5. **Cupric sulfide** and **cupric bromide** lose sulfur and bromine, respectively, when heated, being reduced to the cuprous condition. **Cupric iodide** and **cyanide** are even less stable, for they decompose spontaneously in solution, forming insoluble cuprous iodide and cyanide (§ 537).

6. A double salt, copper arsenite-acetate, commonly called **Paris green,** is used as a poison for destroying leaf-devouring insects (§ 320).

EXERCISES

1. Give equations for the principal reactions taking place when a hydrochloric acid solution, containing potassium chromate, ferric chloride, cupric chloride, and aluminum chloride, is treated with hydrogen sulfide.

2. Give an equation to explain what happens in the roasting of an ore, containing cuprous and ferrous sulfides.

3. Write equations for the chief reactions taking place in a copper converter.

4. The maximum current which will give a smooth deposit of copper in a certain refining bath is about 2 amperes per square decimeter of cathode surface. From the density of copper (8.9) and Faraday's Law (§ 428) determine how long it will take this current to build up a cathode deposit 1 in. (2.5 cm.) thick. (1 decimeter = 10 centimeters.)

5. A flotation concentration plant operates on a copper ore containing 1.4 per cent Cu, producing 1 ton of concentrates for every 15 tons of ore. Assuming 85 per cent of the copper in the ore to be recovered in the concentrates, calculate the percentage of copper in the concentrates.

6. Explain why solutions of cupric sulfate are acid? Give a complete ionic formulation.

7. Describe suitable methods for preparing the following substances from copper sulfate, with equations:

Cupric hydroxide, cupric phosphate, cupric oxalate, cuprous oxide, metallic copper, cupric nitrate.

8. What are the principal impurities contained in blister copper? Which of these are found in the elementary form, in the anode mud. Which pass wholly or in part into solution? Explain (§ 427) how it is possible to secure a deposit of practically pure copper from an electrolyte containing considerable amounts of iron. Does the difficulty in securing a pure deposit increase with increasing concentration of iron in the solution, and if so, why?

9. Cupric hydroxide can be reduced to cuprous oxide by boiling with sodium arsenite solution. Write and balance equation.

10. Give ionic equations to represent all that happens when an excess of ammonium hydroxide is added to a solution containing ferric sulfate, copper sulfate, and sulfuric acid.

11. Making use of the preceding reactions, explain how copper sulfate cyrstals may be tested for iron. (The iron must first be oxidized, if present as ferrous sulfate.) Equation.

12. Give ionic equations to explain why cuprous cyanide dissolves in an excess of potassium cyanide.

13. Three solutions, containing respectively $CuSO_4$, $FeSO_4$, and $Fe_2(SO_4)_3$ are tested with potassium ferrocyanide, metallic iron, and hydrogen sulfide. Describe what happens in each of the nine cases, with equations.

14. Write the formula of a basic copper carbonate, containing twice the quantity of copper for each CO_3 group that would be contained in a salt of normal formula.

15. What connection exists between the fact that solutions of cupric salts react acid and the fact that they give only basic carbonates by precipitation with Na_2CO_3?

16. What is the difference between a double salt and a complex salt? Illustrate.

17. By reference to the text on copper, and by analogy from iron (§ 504) draw up a list of equations showing a number of methods by which cuprous salts can be converted into cupric salts, and conversely.

CHAPTER XLII

SILVER AND GOLD

SILVER

539. Occurrence of Silver.—1. Silver often occurs **native** (§ 415), very commonly in association with gold. A natural alloy of the two metals, known as **electrum,** was considered by the ancients to be a distinct metal, for the separation of its two constituents became possible only with the discovery of sulfuric and nitric acids, in the Middle Ages.

2. **Silver sulfide,** Ag_2S, and **silver chloride,** $AgCl$, in fairly pure condition, are sometimes found in nature, and deposits of these minerals furnish considerable silver.

3. The most important source of silver is found in **the small amounts of silver sulfide that accompany most ores of copper and lead.** When these ores are smelted, the silver alloys with the metallic copper and lead, and is afterward separated from these by a process of refining.

540. Metallurgy of Silver.—At the present time, the world's production of silver is above 7000 tons a year. The United States is the leading producer, furnishing about a third of the total. Mexico is a close second, and Canada comes third. South America has been an important silver-producing region, from the time of Pizarro down to the present day; while most other parts of the world contribute smaller amounts.

1. **Silver from Anode Mud.**—In the electrolytic refining of copper, silver is found in the anode mud (§ 531) as metallic silver, in association with Cu, Cu_2O, Cu_2S, and compounds of As, Sb, Bi, Sn, Pb, Se, Te, etc. This mud is screened to remove coarse particles of anode copper, and is then boiled with dilute sulfuric acid or with dilute acid and silver sulfate solution. This brings most of the impurities into solution, leaving the silver behind as a finely divided metallic residue, which is melted and purified.

2. **The Parkes Process.**—Silver is removed from commercial lead by melting the latter in a large open bath and stirring in 0.8

per cent to 1.5 per cent of its own weight of **zinc,** in two or three successive portions. After each addition, most of the zinc rises to the top of the lead as a scum, which is removed by skimming—for neither metal is very soluble in the other. Most of the silver originally present in the lead is brought to the top in solution in the zinc, and is removed in the operation of skimming, much of it being there present as a definite chemical compound, Ag_2Zn_5. But all the silver cannot be removed from the lead by extraction with zinc, even though the operation be repeated many times, for after each extraction the concentration of the silver remaining in the lead bears a definite ratio to that of the silver in the zinc layer above.

We have here an illustration of a very important generalization called the ***Distribution Law.*** **Whenever two mutually immiscible solvents dissolve a small amount of a third substance the concentrations of the two solutions thus formed will (usually) bear a definite ratio to each other at any given temperature** (regardless of the relative amounts of the two solvents or the actual weight of solute dissolved).

The zinc scums from the desilverization pots are first gently heated, to melt out any adhering lead, which is drained away. The residue is then strongly heated, when the zinc distils away, leaving the silver behind, alloyed with a little gold and small quantities of other metals.

3. **The Cyanide Process.**—Though much more than half the silver now produced comes from the two metallurgical processes just described, there are a great many others that have been employed in the treatment of silver ores. Of these, the one of greatest present importance is the cyanide process. Some of the important Mexican ores consist of quartz rock, carrying small amounts of silver sulfide, Ag_2S.

(*a*) The ore is finely powdered in a *stamp-mill*, and treated with *sodium cyanide* solution in the presence of air:

$$Ag_2S+4NaCN \rightleftarrows 2Na\cdot Ag(CN)_2+Na_2S.$$

(*b*) The reaction is reversible and hence remains incomplete unless the sodium sulfide formed is removed by oxidation with air or by precipitation with a compound of lead or mercury:

$$2Na_2S+H_2O+2O_2 \rightarrow Na_2S_2O_3+2NaOH,$$
$$Na_2S+PbO+H_2O \rightarrow 2NaOH + PbS \downarrow .$$

(*c*) The soluble salt of silver thus formed (sodium argenticyanide) contains silver in the complex anion (§ 536), $Ag(CN)_2^-$, which is decomposed with metallic zinc, and the silver precipitated:

$$2Na \cdot Ag(CN)_2 \rightleftarrows 2Na^+ + 2Ag(CN)_2^-$$
$$Zn + 2Ag(CN)_2 \longrightarrow Zn^{++} + 4CN^- + 2Ag\downarrow .$$

Explain this reaction as a transfer of electrons. Give a molecular equation to represent it as a reaction between metallic zinc and molecules of $Na \cdot Ag(CN)_2$.

541. Properties and Uses of Silver.—The most noteworthy properties of metallic silver are its freedom from rusting, high luster, malleability, and ductility. It has been beaten out so thin that several hundred sheets would be needed to make a layer the thickness of a leaf of this book; and the silver in a dime, if drawn into wire, could be made to extend more than a mile.

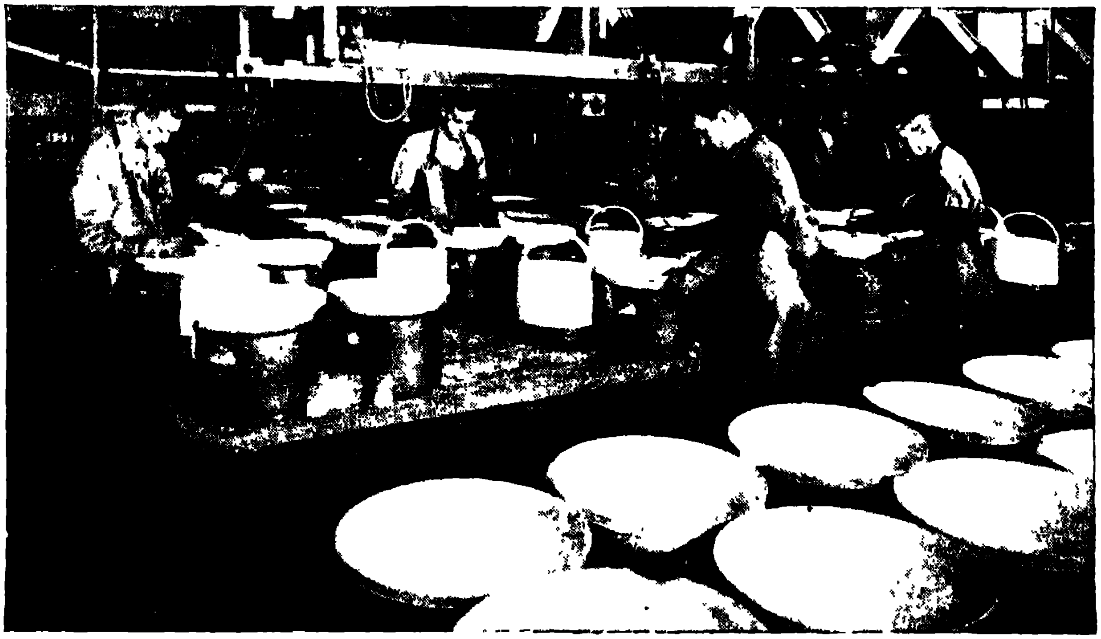


FIG. 124.—Recrystallizing silver nitrate, to be used in preparing silver bromide, for coating photographic films. Note that the workmen use rubber gloves and rubber aprons, for silver nitrate, though neutral to indicators, is highly caustic to the skin

These physical properties of silver, together with its resistance to most acids and freedom from rusting, make it an exceedingly useful metal. Thousands of tons are used each year for coinage, for the manufacture of jewelry, and for decorative purposes. Silver plating, the manufacture of mirrors, and the photographic industries call for further quantities.

542. Chemical Properties of Silver.—The relationship of silver to copper is shown not only in its physical properties—malleability, ductility, excellent thermal and electrical conductivity, high melting point—but in a number of its chemical characteristics:

1. **Its halogen compounds** (except AgF), like the corresponding cuprous salts, **are insoluble in water.**

2. **Silver salts,** like cuprous salts, **are precipitated by ammonium hydroxide and potassium cyanide, but redissolve in an excess of the reagent, giving complex salts, $Ag(NH_3)_2 \cdot Cl$ and $K \cdot Ag(CN)_2$.** (Note that in one of these silver is in the cation; and in the other in the anion.)

But there are some striking **differences** between the two metals:

3. **Silver has the valence one in all its salts, whereas copper has that valence only occasionally,** its most important compounds being those in which it is bivalent.

4. **Cuprous oxide is insoluble in water. Silver oxide has a slight, but very appreciable, solubility, forming a solution with an alkaline reaction.**

$$Ag_2O + H_2O \rightleftarrows 2AgOH.$$

5. **Silver salts are very much less hydrolyzed by water than those of copper.** Thus, silver nitrate solutions are neutral toward litmus, while solutions of cupric nitrate are definitely acid. Again, silver forms a normal carbonate, by interaction of solutions of $AgNO_3$ and Na_2CO_3; but with copper we can obtain only a basic carbonate, such as $Cu(OH)_2 \cdot CuCO_3$.

543. Silver Plating.—Articles are usually plated with silver by being made cathode (Fig. 125) in a solution of the complex salt—**sodium argenticyanide, $Na \cdot Ag(CN)_2$** (§ 540, item 3)—formed by adding an excess of sodium cyanide to a solution of silver nitrate:

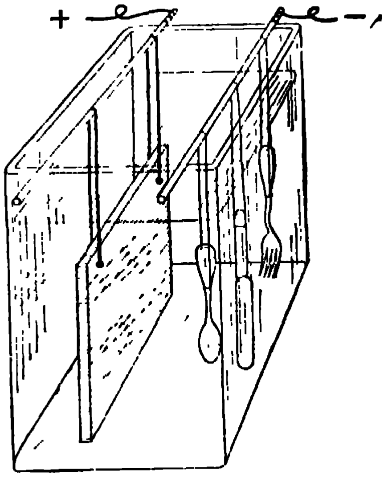
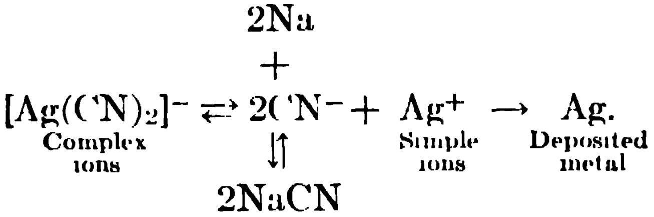


Fig. 125.—Electroplating tableware in a bath of sodium argenticyanide The anode is a plate of pure silver.

$$NaCN + AgNO_3 = \underset{\text{Precipitated}}{AgCN \downarrow} + NaNO_3,$$

$$NaCN + AgCN = \underset{\text{Redissolved}}{Na \cdot Ag(CN)_2}.$$

Though most of the silver in such a solution is assumed to be present as the complex negative argenticyanide-ion, $[Ag(CN)_2]^-$, and accordingly moves toward the anode during electrolysis, a very small part is present as Ag^+ ions, which migrate toward the cathode, and are there deposited:



$$\underset{\text{Complex ions}}{[Ag(CN)_2]^-} \rightleftarrows \begin{array}{c} 2Na \\ + \\ 2CN^- \\ \downarrow\uparrow \\ 2NaCN \end{array} + \underset{\text{Simple ions}}{Ag^+} \longrightarrow \underset{\text{Deposited metal}}{Ag.}$$

Silver deposited from such a cyanide bath is *smooth*, while that from a nitrate bath is *coarsely crystalline* and *non-adherent*. The reason for this has not been completely explained. It seems likely that the metal in either case is first deposited in an amorphous (non-crystalline) form; but that conditions in the nitrate bath favor its alteration into crystals. For the electrodeposition of metals in general, it is found that **a smooth deposit is commonly favored by the presence of complex ions, by traces of colloidal substances, such as glue (§ 533), by stirring the electrolyte, by rotating the cathode, and by using reasonably heavy currents.**

544. Silvering Glass.—In silvering mirrors and Dewar flasks the glass surface is first very thoroughly cleaned, then covered with an ammoniacal silver nitrate solution, made strongly alkaline with potassium hydroxide, and containing a small amount of some freshly added reducing agent (glucose or formaldehyde). In a few minutes the surface becomes covered with a bright film of reduced metallic silver. Solutions that have once been used should be poured into jars containing common salt, in order to recover the silver as chloride, which may afterward be reduced to spongy metal by reduction with granulated zinc and sulfuric acid. If the silvering solutions are permitted to stand for a few hours, silver fulminate, AgONC, may be formed; this is an extremely dangerous substance, exploding violently at the slightest touch.

545. Use of Silver Halides in Photography.—Photographic films are prepared from cellulose nitrate (§ 370) and coated with an emulsion of silver bromide and gelatin. When such a sensitized film or plate is exposed to the light—even for so little as a thousandth of a second—some subtle change takes place in the silver salt, making it more easily reduced to metallic silver than before. To the eye, such an exposed film appears precisely like one that has not been exposed; yet when it is placed in a solution of an **organic reducing agent,** commonly called a ***developer,*** the portions previously illuminated flash out in dark metallic silver, while the rest of the film retains the yellow tint of unchanged silver bromide.

After development, the films or plates are rinsed with water and transferred to a ***fixing-bath,*** containing **sodium thiosulfate.** This salt has the ability to dissolve silver bromide, and in a few minutes all of the latter that has escaped reduction is completely removed, leaving behind the **negative** picture in metallic silver. The object of removing the excess silver bromide is to prevent it from being darkened by subsequent exposure to light, for if this should happen all parts of the picture would take on about the same shade.

Light and darkness are reversed in the negative, for all the brighter parts of objects photographed are represented in it by dark patches of metallic silver. But in the final **prints,** made from the negative on paper sensitized with one of the silver halides, and developed and fixed in much the same way as the negative itself, a second reversal is accomplished, and light and darkness appear in their true relations.

546. Analytical Tests for Silver.— It is customary to test for silver in solution by the addition of dilute hydrochloric acid or a soluble chloride, which forms a curdy, white precipitate of **silver chloride, AgCl.** This is readily soluble in ammonium hydroxide.

$$AgCl + 2NH_4OH = AgCl \cdot 2NH_3 + 2H_2O.$$

Silver is supposed to exist in this solution as the complex ion, $[Ag \cdot 2NH_3]^+$.

Silver bromide is an insoluble salt with properties very similar to those of silver chloride, but it is pale yellow, instead of white. **Silver iodide** is a deep lemon-yellow precipitate, and differs from the chloride and bromide in being insoluble in ammonium hydroxide.

Silver chromate is a red precipitate, and **silver sulfide** a brownish-black one.

Silver fluoride, remarkably enough, differs from the chloride, bromide, and iodide in being soluble in water. In fact, *the fluoride, nitrate, and chlorate are the only readily soluble, inorganic silver salts.* The sulfate, acetate, and bromate are sparingly soluble.

GOLD

547. Metallurgy of Gold.—Gold is generally found in the free state, **as grains or nuggets,** in alluvial sand; or **in a finely subdivided condition, in veins of quartz.** A deposit of **gold and silver, in association with tellurium and lead** (so-called gold telluride) was of considerable importance a generation ago in the famous telluride mines of Colorado.

This remarkable ore, after concentration by simple mechanical means, contained up to 10 per cent gold, and was valued at as much as $50,000 a ton. Auriferous quartz, however, can be profitably mined when it contains only a small fraction of an ounce in each ton, and gold-bearing gravel when it contains as little as one part of precious metal in several million parts of gangue.

1. **Hydraulic Mining.**—Gold is between seven and eight times as heavy as the minerals with which it is commonly associated, and is therefore easily separated from alluvial deposits by a process of washing with water (hydraulic mining, sluicing).

2. **Amalgamation Process.** Gold-bearing quartz rock is put through stamp-mills to reduce it to a fine powder, and is then floated with water over a series of copper plates, covered with mercury. (Mercury will stick to copper that has been cleaned with acid.) A considerable part of the gold in the powdered ore amalgamates with the mercury (§ 561) which is scraped off the plates from time to time, and distilled. The residue of impure gold thus obtained, containing silver, copper, and smaller quantities of other metals, is often purified by electrolysis.

3. **Chlorination Process.**—Gold may be extracted from certain rich ores by a roasting to expel sulfur and arsenic, followed by treatment with chlorine gas in the presence of moisture. This brings the gold into solution as auric chloride, $AuCl_3$. The solution is filtered, and the metal thrown down by treatment with some reducing agent, commonly ferrous sulfate.

4 **Cyanide Process.**—Most of the **tailings,** or extracted ore, from the amalgamation process, will contain enough gold to pay

for extraction with sodium cyanide. The process must be carried out in the presence of air, as in the cyanide process for extracting silver (§ 540); but it is simplified by the fact that the gold is present in the metallic condition, rather than as a sulfide:

$$4Au+8NaCN+2H_2O+O_2=4NaOH+4NaAu(CN)_2.$$

The gold is separated from the solution thus obtained by precipitation with metallic zinc or by electrolysis. The cyanide remaining in the solution is used to extract a fresh supply of ore.

About half of the world's production of gold now comes from South Africa, about one-sixth from the United States, and the remaining third from many widely scattered sources. The development of the cyanide process, described in the preceding section, has greatly increased the production of both gold and silver, within recent years. At the present time, the total annual output is over 600 tons of gold, and about a dozen times that amount of silver (1922).

Such a flood of precious metal was never known before. The pages of history are full of romantic stories about the stores of wealth taken from Mexico and South America in days gone by, when pirates swarmed in all the tropical seas, and Drake and Hawkins ran down treasure ships upon the Spanish Main. Yet statistics seem to show that the world now actually produces as much gold in three years, and as much silver in ten, as came from all the mines of the Western Hemisphere in the three centuries following its discovery.

548. Gold as the Standard of Value.—There was some reason for the esteem in which gold was held in ancient times; for it could be had in fair abundance, without recourse to complicated metallurgical processes, was easily worked, and was of an imperishable nature, entirely proof against loss by fire, rusting, or corrosion. These circumstances combined to establish it as a standard of value and medium of exchange among primitive peoples, a position it has held, against all reason, down to this very hour.

In competition with other metals available to men of the twentieth century, gold is, however, but a poor material. Its ductility is hardly superior to that of tungsten, and it is by no means so strong. Its malleability is not much greater than that of silver, and it is far scarcer. It is too soft to withstand any ordinary wear, unless toughened by addition of copper. It is no more beautiful than aluminum bronze, has less mechanical strength, and is inconveniently heavy. Another consequence of its high specific gravity is that gold-plating of any serviceable thickness becomes needlessly costly. Its electrical conductivity is inferior to that of copper and silver, and its resistance to chemicals inferior to that of platinum. It has very little tensile strength, cannot be hardened by any known process of tempering or annealing, and shrinks too much in solidifying to be usefully cast. None of its alloys have any unique properties, and its compounds have no important use. We should get along very nicely if all the gold in the world were to disappear to-morrow; yet the caprice of history has made this practically useless element the standard by which we measure the value of such indispensable things as copper, iron, coal, and electrical energy.

549. Chemical Properties of Gold.—Metallic gold does not rust or tarnish in the air, and does not dissolve in any of the dilute acids, nor even in any of the oxidizing acids (except selenic acid). It does unite directly, however, with the free halogens, and for this reason is dissolved by *aqua regia* (a mixture of HCl and HNO_3, § 301), and even by boiling solutions of ferric chloride and bromide. The most important solvent for gold is sodium cyanide, in the presence of air (§ 547).

Gold forms halides in the valences *one* and *three,* e.g., aurous chloride, AuCl; and auric chloride, $AuCl_3$. But very few other salts are known in which it plays the part of a metal. Its most important compounds are those in which it forms part of a non-metallic radical: potassium aurate, $K \cdot AuO_2$; and potassium aurocyanide and auricyanide, $K \cdot Au(CN)_2$ and $K \cdot Au(CN)_4$, solutions of which are used in gold-plating baths.

EXERCISES

1. In extracting anode mud with dilute sulfuric acid, explain why silver fails to dissolve, though it does dissolve in the parting process, when a gold and silver alloy is treated with hot concentrated sulfuric acid.

2. Explain why even dilute nitric acid will dissolve no silver from anode mud, so long as this contains particles of metallic copper.

3. What impurities, likely to be present in commercial silver, would you expect to be able to remove by dissolving the metal in dilute nitric acid, and reprecipitating with strips of sheet copper? Explain.

4. How would you prepare the arsenate, chromate, phosphate, iodide, and sulfide of silver?

5. Write equations to show the effect, if any, of strongly heating each of the following substances in a Bunsen flame: Cupric nirate, silver sulfate, ammonium sulfate, barium sulfate.

6. Write ionic and molecular equations for the reduction of auric chloride to metallic gold by ferrous sulfate solution.

7. What is the action of hydrogen on heated copper oxide? Describe how this reaction may be used to determine the quantitative composition of water by weight.

8. Write and balance equations for the solution of copper in nitric acid and in hot concentrated sulfuric acid. Under what circumstances will copper dissolve in dilute sulfuric acid?

9. Photographic prints are sometimes toned by being dipped in gold chloride solution. By this means the dark deposit of metallic silver is given a brighter tint. Explain, with an equation.

10. Explain the following terms used in this and the preceding chapter: Metallurgy, alluvial, auriferous, concentrates, matte.

CHAPTER XLIII

ZINC, CADMIUM, AND MERCURY

Next to iron and copper, the most important metals are zinc and lead. These happen to fall in two different groups of the periodic table, and are therefore, described here in separate chapters, although they have many properties in common.

Zinc has been known since the Middle Ages, but is a distinctly modern element, for it is only within the past century that important uses for its compounds have been developed, and the virtues of the metal itself properly appreciated. It occurs in group II B of the Periodic Table, along with mercury and cadmium.

Mercury is of less importance, but in some of its applications—as in the preparation of pigments and the extraction of gold from its ores—has been in use for many centuries. *Cadmium* is of minor economic value. The three metals, zinc, cadmium, and mercury, share certain chemical traits, but we shall find that differences are quite as striking as resemblances; and that mercury, in particular, possesses characteristics that ally it to the preceding group of the periodic table, containing copper, silver, and gold.

ZINC

550. Occurrence of Zinc.—The most important ores of zinc are (1) the sulfide, called **sphalerite, " black jack," or zinc blende;** (2) zinc orthosilicate, Zn_2SiO_4, which is commonly known as calamine; (3) zinc carbonate, or smithsonite; (4) **franklinite,** a mineral consisting of zinc oxide, in combination with varying proportions of the oxides of iron and manganese (in valences two and three). These minerals usually occur together in nature, and are commonly associated with compounds of lead and cadmium. But the deposit of franklinite, in New Jersey, is nearly free from both of these metals, and the zinc produced from it by simple reduction with carbon is generally above 99.9 per cent pure.

551. Metallurgy of Zinc.—Zinc is obtained from its ores by very simple metallurgical processes, which have remained almost unimproved since their first development, almost a century ago. The concentrated ore is **roasted,** to oxidize and remove sulfur and arsenic, if it contains any considerable percentage of these elements. It is then **heated with anthracite coal in a small fur-**

nace, to which compressed air is supplied beneath grates at the bottom. The roasted ore is reduced by the carbon monoxide to metallic zinc, which distils away as vapor and is condensed in earthenware receivers (boiling point of zinc, 925° C.). The residue, if the ore was franklinite, consists largely of ferrous and manganous oxides, and may be reduced in a blast furnace, for the production of manganese-iron alloys (§ 514).

The United States (New Jersey, Missouri, Idaho, Utah, Colorado) now produces about half of the world's supply of zinc, which has been as much as a million tons a year.

ZINC ORE

Zinc Dust	Spelter	Zinc Oxide	Zinc Chloride
Manufacture of dyes	Sheet zinc	Cosmetics	Wood preservative
Sherardizing	Roofing	White rubber	Dry cells
Marine paints	Gutter pipe	Tires	Soldering
Purifying zinc liquors	Dry cells	Enameled ware	Manufacture of dyes
	Nails	Printing inks	
Cyanide process for Au and Ag	Zinc etchings	Glues	Vulcanized fiber (§ 375)
	Mossy zinc	Dental cements	
	Soot cleaner	Artificial teeth	→ Zinc Sulfate
			Glue
	Feathered zinc	Imitation ivory	
			Cold galvanizing
	Recovering Ag from solutions	Glazes	
		Matches	Preparing cement for painting
	C.P. granular zinc	Abrasion wheels	
	Laboratory reagent	Porcelain	Cotton printing
	Brass	Glass	Lithopone
	Galvanized iron	Oilcloth	
		Linoleum	

552. Uses of Metallic Zinc.—1. The vapors that issue from the zinc-reduction furnaces at first condense in the receivers as a very fine metallic powder, called **zinc dust,** containing a few per cent of zinc oxide. This is important as a **reducing agent** in the manufacture of dyestuffs, synthetic drugs, and perfumes (§ 374). Large quantities are also used in **precipitating gold and silver in the cyanide process** (§ 547). Steel is frequently protected against corrosion by being thoroughly cleaned, then heated for several hours in closed drums in contact with zinc dust (§ 503). A thin coating of an alloy of zinc and iron is thus produced. The process is called **sherardizing,** one of its important applications being the protection of the steel conduits in which telephone cables are laid in most of our large cities.

2. Commercial zinc is commonly called **spelter.** It is too brittle to be worked at room temperature, but can be rolled out between heated rollers, at 150° to 200°. For roofing, gutter-pipe, and the like, sheet zinc has the advantage over steel of being very resistant to corrosion. The only effect of the atmosphere, under ordinary conditions, is to cover the material with a uniform coating of basic carbonate, which sticks tightly to the metal beneath, protecting the latter from any further corrosion.

Sheet zinc is also consumed in enormous quantities in the manufacture of dry cells (§ 425). We have already mentioned its use in recovering silver in the Parkes Process (§ 540). Other uses are shown in the preceding diagram.

3. One of the most important uses of metallic zinc is in the manufacture of **galvanized iron and steel.** The sheet metal is thoroughly cleaned, by sand blasting or by pickling in dilute sulfuric acid, and is then dipped in a bath of molten spelter. The surface of the sheet is thus covered with a very thin coating of zinc, usually in beautiful crystalline patterns that put one in mind of frost tracings on the windows in winter time. Objects that would be injured by the heat of the galvanizing bath are sometimes coated with zinc by an electroplating process.

4. The most important alloy of zinc is **brass** (§ 532); but zinc is a constituent of many bronzes, and is sometimes melted with aluminum to form tough, light alloys having properties and uses similar to those of magnalium (§ 418).

553. Zinc Oxide.—Zinc oxide is sometimes produced on a large scale by distilling metallic zinc in a current of air. The vapors catch fire and burn with a bluish flame, yielding white fumes of zinc oxide (French process). In New Jersey zinc oxide is made directly from the ore. This is reduced to metal by means of anthracite coal in the usual way; but the vapors escaping from the top of the furnace, instead of being condensed, are mingled with an excess of air, and burn directly to oxide.

Zinc oxide produced by either of these two methods is in *a very finely divided condition*— a property which makes it valuable as a paint pigment. Enormous quantities are also used as a filler for rubber (§ 353) in the manufacture of automobile tires. Large quantities are consumed in the manufacture of enamels and glazes and laboratory glassware (§ 408). The total production of zinc oxide, in the United States alone, now amounts to more than 100,000 tons a year.

554. Paints and Paint Pigments.—The use of zinc oxide as a paint pigment calls for a few words concerning paints and paint pigments in general. **A good paint consists of at least three ingredients:**

First, an **opaque pigment** or **body,** having great capacity for reflecting the light, and consequently great capacity for covering up and hiding the surface on which it is spread. The best substances for this purpose are basic lead carbonate (§ 580), basic lead sulfate (§ 580), and zinc oxide.

Second, an **inert filler** or **extender,** such as barium sulfate, chalk, or China clay (§ 483). Such a substance in itself has no great " covering power "; but it may be added to the main pigment in a small proportion, to prevent the latter from being spread out too thin, and in some cases to make it cling better to the surface on which it is spread.

Third, a **vehicle,** or **medium**—a drying oil (§ 362). The pigment and filler are incorporated in this by means of special grinding machinery, that reduces the particles to the utmost possible degree of subdivision, and produces a homogeneous, viscous mass needing only to be thinned with a small amount of turpentine, boiled linseed oil, or naphtha (§ 352) to be ready for use. The vehicle must dry by oxidation within a reasonable time, and must be free from more than traces of acid. Pure linseed oil is best, though the admixture of a small amount of turpentine is permitted.

In addition to these three constituents, a **colored pigment** needs to be added if the paint is to be of any other shade than white.

Among the opaque pigments, each has some special virtues. Zinc oxide is pure white, is non-poisonous, and will not darken when exposed to air containing hydrogen sulfide (since ZnS also is white). But zinc oxide paints have the disadvantage of drying in films that tend to blister and peel off. The white lead paints have the opposite failing, tending to become chalky, and hence easily rubbed off, after long exposure to the air. Another disadvantage of this chalky texture is that it hinders the removal of dirt by sponging. Zinc oxide paints are distinctly inferior to white-lead paints in covering power. Because of its cheapness, however, zinc oxide has been used to a large extent as an adulterant of white lead. Paint manufacturers are now required by law to state the composition of their products.

555. Uses of Zinc Salts.—All zinc salts are poisonous. A solution of zinc chloride is thus used for treating railroad ties, to discourage the growth of wood-destroying fungi. We have already mentioned the use of this solution as a solvent for cellulose and in preparing fiberloid (vulcanized fiber, § 370). Zinc sulfate solution is a mordant in cotton printing (§ 372). It is brushed over surfaces of cement or plaster to close the pores in preparation for painting, and is used as an antiseptic in making up glue solutions.

Lithopone (or albalith) is a mixture of barium sulfate and zinc sulfide formed by double decomposition:

$$ZnSO_4 + BaS = BaSO_4 \downarrow + ZnS \downarrow .$$

The mixture of the two insoluble salts is reduced to an extremely fine state of subdivision by a special treatment involving heating to redness and quenching in cold water, and makes a serviceable pigment in dull or flat-finish white paints, for interior decoration.

556. Chemical Characteristics of Zinc.—Zinc is a typical heavy metal, forming salts which are of considerable stability in the dry anhydrous condition, but which are somewhat readily hydrolyzed by water. Solutions of zinc salts of all the active acids accordingly redden blue litmus:

$$ZnCl_2 + HOH \rightleftarrows Zn(OH)Cl + HCl.$$

On evaporating such a solution, the acid will often be volatilized, and the basic salt left behind; or, if the water lost by evaporation is continually replaced, the final result may be a colloidal solution of zinc hydroxide.

The fact that zinc oxide dissolves in dilute acids to form salts (sulfate, nitrate, acetate, etc.) shows it to be of a definite base-forming character. On the other hand, it is easily dissolved by strong bases, forming so-called zincates. The dissolving of zinc oxide (or zinc hydroxide) in sodium hydroxide is commonly formulated:

$$ZnO+2NaOH=\underset{\text{Sodium zincate}}{Na_2ZnO_2}+H_2O.$$

Nevertheless, there is evidence that we have here, in part, to deal with a case of colloidal dispersion or peptization (§ 390) and not with the formation of a definite chemical compound at all.

557. Analytical Tests for Zinc.—There is no characteristic color test by which zinc compounds may be identified in solution.

(1) **But if other heavy metals are absent or have been removed by appropriate precipitating agents, zinc may be recognized by the *white precipitate*, ZnS, which it gives with hydrogen sulfide, in alkaline, neutral, or faintly acid solutions.** (Write equation.) This reaction is reversible, and if the solution contains even small concentrations of the more active acids (such as HCl) zinc will fail to precipitate. In such a case, the hydrogen ion concentration must be reduced by the addition of sodium acetate.

(2) Zinc is also occasionally identified in neutral solutions, in the absence of iron (§ 505), or large quantities of copper (§ 537), by the white precipitate of zinc ferrocyanide which zinc salts give with potassium ferrocyanide solution. (Write equation.)

(3) Another test for zinc depends on the fact that when a zinc compound is mixed with sodium carbonate, moistened with a solution containing a *mere trace* of cobalt nitrate, and fused on platinum or charcoal, a characteristic green color is produced, commonly assumed to be cobalt zincate (**Rinmann's green**). Compare with the test for aluminum (§ 480).

$$Na_2CO_3+Co(NO_3)_2=CoCO_3\quad+2NaNO_3,$$
$$CoCO_3+ZnCO_3\quad=\underset{\text{Cobalt}}{Co(ZnO_2)}+2CO_2.$$

CADMIUM

558. Occurrence, Preparation, and Uses.—Cadmium occurs in small quantities in almost all ores of zinc, and is obtained as a by-product in the smelting of the latter. It is somewhat more volatile than zinc and is therefore collected very largely in the first portions of metal to distil from the zinc reduction furnaces. By repeated fractional distillation, followed by solution in sulfuric acid, and electrolysis of the sulfate solution thus prepared, the cadmium may be obtained pure. If the demand were sufficient, several thousand tons of cadmium could thus be obtained each year from zinc now mined.

Metallic cadmium is chiefly used for making low-melting alloys for electric **fuses** and automatic sprinkling systems for fire-control. An alloy called Wood's metal (50 per cent Bi, 25 per cent Pb, 12.5 per cent Sn, 12.5 per cent Cd) melts at 65° C. Carefully purified cadmium is used in **standard cells** (for measuring electromotive force). **Cadmium sulfide** is a fine lemon-yellow pigment, used in paints and artists' colors.

559. Chemical Characteristics of Cadmium.—Cadmium resembles zinc in being bivalent (§ 119) in all its compounds. Its hydroxide, like that of zinc, dissolves in an excess of ammonium hydroxide; but, unlike zinc hydroxide, fails to dissolve in an excess of sodium hydroxide. Cadmium sulfide, unlike zinc sulfide, is precipitated by hydrogen sulfide in solutions containing dilute HCl or H_2SO_4 (about N/4). Cadmium salts are less readily hydrolyzed than those of zinc, and solutions containing them are generally neutral toward indicators.

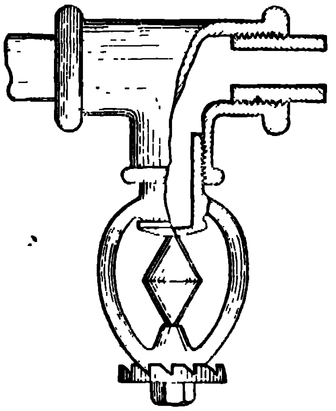


FIG 126.—An automatic sprinkler. A pointed plug of cadmium alloy melts at about 65° C., and releases a jet of water.

MERCURY

560. Occurrence, Preparation, and Purification.—The chief producers of mercury, in the order named, are the United States, Spain, and Austria. The principal ore is **cinnabar,** or mercuric sulfide, HgS, which forms dark red crystals. When this is roasted in a current of air, the sulfur is burned away, while the mercury vapors may be condensed and collected as liquid metal. Sometimes the ore is heated with quicklime in closed retorts, forming calcium sulfide, metallic mercury, and oxygen.

561. Uses of Metallic Mercury.—Metallic mercury is used in barometers, thermometers, and high-vacuum air pumps, in extracting gold from its ores (§ 547), and in preparing dental alloys. The largest refracting telescope in the world, weighing 95 tons, at the Mount Wilson observatory in Southern California, is balanced in metallic mercury and is thus very easily manipulated in spite of its great weight.

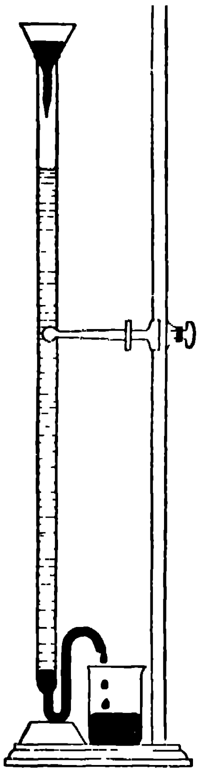


FIG. 127.—Purifying mercury. A fine stream of mercury is sprayed through a column of dilute nitric acid, containing a little mercurous nitrate. Metallic impurities above mercury in the electrochemical series are dissolved. Note how the short column of mercury, in the siphon at the bottom of the apparatus, balances the long column of nitric acid. Mercury may also be purified by distillation in a vacuum.

An alloy of mercury with any other metal is called an **amalgam.** Sodium amalgam is used as a reducing agent in preparing a number of important organic compounds. The mercury arc lamp makes use of the fact that a bluish light, rich in ultra-violet rays, is emitted when an electric discharge takes place through mercury vapor. Mercury arc rectifiers are in common use in automobile service stations, for charging storage batteries.

562. Some Important Compounds of Mercury.— **Calomel,** or mercurous chloride, HgCl, is a white insoluble salt, sometimes given in small doses as an intestinal antiseptic in cases of digestive derangement.

Corrosive sublimate, or mercuric chloride, $HgCl_2$, in contrast to calomel, is readily soluble in water, and is an exceedingly dangerous poison. A solution containing one part mercuric chloride in a thousand of water is used externally as a sterilizing wash in surgical technique. Somewhat stronger solutions are used for preserving botanical and anatomical specimens. Large quantities of mercuric chloride are used for disinfecting and preserving the materials used in the fur and felt-hat industries.

Mercuric sulfide is black when made by precipitation or by rubbing sulfur and mercury together; but it becomes a bright red when sublimed or when digested with a solution of an alkali sulfide. In the red form it is identical with the mineral cinnabar, and has been used for centuries as an artists' pigment, under the name of **vermilion.**

Mercuric fulminate, $Hg(OCN)_2$, is a white powder, used universally as a primer in small-arms ammunition. This explodes when struck, and the concussion sets off the main charge of smokeless powder (nitrocellulose, § 370). Mercury is a constituent of a number of important synthetic drugs.

Mercuric iodide, HgI_2, an insoluble red or yellow salt, dissolves in an excess of potassium iodide solution to form a soluble complex salt, potassium mercuric iodide, K_2HgI_4. Mercury, here, is in the complex anion $(HgI_4)^{--}$.

563. Precautions in the Use of Mercury and Mercury Salts.—**All soluble mercury salts are extremely poisonous.** With corrosive sublimate, the fatal dose may be less than 200 mg. **The antidote is milk or raw white of egg,** which precipitates insoluble mercuric compounds—so-called mercury albuminates.

Quantities of mercury far too small to produce immediate manifestation of poisoning are distinctly dangerous, because they are retained almost indefinitely in the system and, by accumulation, may lead to chronic mercury poisoning—a disorder marked by ulcerous inflammation of the gums and other loathsome symptoms.

Whenever the least amount of metallic mercury happens to be spilled in the laboratory, it should be swept up immediately. If permitted to lie around, it will become more and more finely divided, the droplets being prevented from reuniting by a layer of adsorbed dirt or grease. Presently a stage of subdivision may be reached which will permit the metallic particles to float in the air.

Never pour solutions of mercury salts into the laboratory sinks. They will ruin the lead plumbing. A waste-jar, containing granulated zinc, should be provided.

564. Chemical Characteristics of Mercury.—Although mercury is in the same column of the periodic table with zinc and cadmium, its chemical properties relate it rather to copper. Thus, like copper, it fails to dissolve in dilute non-oxidizing acids,* but is readily brought into solution by nitric acid or hot concentrated sulfuric acid. Like copper, also, **mercury forms two series of salts, in which it is respectively univalent and bivalent;** but mercurous salts have been prepared in many cases in which the corresponding cuprous salts are either unknown or decomposed by water.

1. **Mercury salts of both types are easily hydrolyzed,** and their solutions accordingly have an acid reaction. In fact, solutions of mercurous nitrate and mercuric nitrate in dilute nitric acid, on being diluted with water, precipitate insoluble basic salts:

$$2HgNO_3 + HOH \rightleftarrows Hg_2(OH)NO_3 \downarrow + HNO_3.$$

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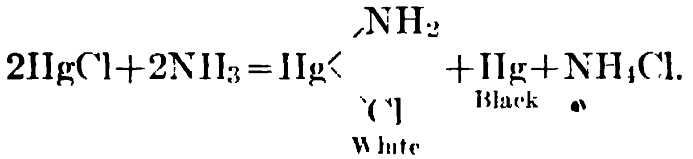
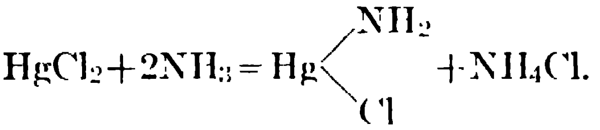
* Mercury dissolves in hydriodic acid, because of the stability of the HgI_4^{--} anion (§ 562).

On boiling dilute solutions of mercuric salts, hydrolysis occurs, and mercuric oxide is thrown down. **No hydroxide or carbonate of mercury is known.**

2. **Mercurous chloride and mercuric chloride, on being treated with ammonium hydroxide, both yield white *mercuric amido-chloride*, HgNH$_2$Cl;** but in the former case the precipitate is colored black from the separation of metallic mercury in finely divided condition—a fact used to distinguish HgCl from AgCl (§ 542 item 2):



$$2HgCl+2NH_3=\underset{\text{White}}{Hg\begin{cases}NH_2\\Cl\end{cases}}+\underset{\text{Black}}{Hg}+NH_4Cl.$$



$$HgCl_2+2NH_3=Hg\begin{cases}NH_2\\Cl\end{cases}+NH_4Cl.$$

Other mercury salts form similar compounds (as Hg(NH$_2$)NO$_3$) when treated with ammonium hydroxide.

3. **Mercuric salts are easily reduced to mercurous salts by contact with metallic mercury:**

$$HgSO_4+Hg \rightleftarrows Hg_2SO_4.$$

If a small amount of stannous chloride is added to a solution of a mercuric salt, the latter is reduced, and a white precipitate of calomel thrown down:

$$2\underset{\text{(Excess)}}{HgCl_2}+SnCl_2=SnCl_4+2HgCl\downarrow.$$

But if the stannous chloride is used in large excess, the precipitate will be gray or black, from separation of metallic mercury:

$$HgCl_2+\underset{\text{(Excess)}}{SnCl_2}=SnCl_4+Hg\downarrow.$$

4. **The halides and sulfides of mercury sublime when strongly heated.** Mercuric chloride is so volatile, indeed, that it passes off with the steam when its solution is boiled. When mercury salts containing oxygen are ignited, they are decomposed, liberating metallic mercury.

EXERCISES

1. Write equations for roasting and reduction of a zinc sulfide ore.

2. Give balanced ionic equations for the following:

(*a*) Liberation of hydrogen by action of zinc dust on an alkali.

(*b*) Precipitation of silver from a solution of sodium argenticyanide by metallic zinc.

(*c*) Testing for zinc in a zinc sulfate solution by potassium ferrocyanide.

(*d*) Precipitation of zinc as zinc sulfide from an acetate solution.

(*e*) Purification of a zinc chloride solution containing a small amount of cupric chloride.

3. What methods, other than galvanizing, are in use for protecting iron and steel against corrosion?

4. A solution containing copper, zinc, and cadmium sulfates is electrolyzed, with a gradually increasing electromotive force. In what order will the metals be deposited? State the principle involved (§ 127).

5. What weight of spelter will be needed to galvanize a ton of sheet steel, assuming no loss, the average thickness of the coating *on each surface* of the sheets being 2 per cent of the thickness of the sheets themselves? Sp. gr. of steel is 7.85 and of zinc is 7.05.

6. Zinc is sometimes brushed over with a solution of cupric acetate, in order to roughen its surface, in preparation for painting. State the chemical action involved.

7. The quality of galvanizing on sheet metal is sometimes estimated by treating a known area with concentrated hydrochloric acid, containing a little $SbCl_3$, and noting the volume of hydrogen evolved. The acid dissolves the zinc very quickly, but attacks the underlying steel only very slowly. In one such test, an area of 20 sq. cm. yielded 220 c.c. of hydrogen gas, measured over water at 20° C. and 740 mm. pressure. Calculate the weight of zinc on the surface, in grams per square meter.

8. Sphalerite is roasted, using 50 per cent more air than is needed. Calculate the percentages of O_2, SO_2 and N_2 in the gases issuing from the furnace.

9. What is the theoretical percentage of zinc in lithopone?

10. Describe the peptization (§ 383) of zinc hydroxide by the caustic alkalies.

11. What must be the price of zinc carbonate, to compete with zinc oxide costing 15 cents a pound, for the production of zinc chloride?

12. From the chemical nature of concrete (§§ 161, 466) and limestone, formulate reactions explaining the use of zinc sulfate solutions in preparing surfaces of such material for painting.

13. What property of zinc salts makes zinc sulfate useful as a mordant?

14. With zinc oxide at 15 cents a pound and commercial 40 per cent hydrochloric acid at 3 cents a pound, calculate the cost per gallon of wood-preservative solution, of specific gravity 1.40, containing 60 per cent $ZnCl_2$. One (U. S.) gallon of water weighs 8.34 lbs.

15. A solution of zinc chloride, when evaporated to dryness, leaves behind a residue of basic salt, while a solution of zinc sulfate produces crystals of the normal salt, $ZnSO_4 \cdot 7H_2O$. Explain.

16. When a few drops of potassium ferrocyanide are added to a solution containing zinc chloride and cupric chloride, a white precipitate is formed. On the addition of a larger quantity of the reagent, the precipitate becomes

red. What conclusion can be drawn concerning the relative solubilities of the ferrocyanides of zinc and copper?

17. How does the ready hydrolysis of zinc salts explain the use of zinc chloride solutions for cleaning oxidized metallic surfaces, in preparation for soldering? In what way is such a solution superior to hydrochloric acid?

B (558–564). 18. Starting in each case with metallic cadmium, how would one prepare: the sulfate, carbonate, cyanide, acetate, sulfide, iodide? Write equations.

19. By what single reagent, added to a solution of the acetate of the metal, could you distinguish:

(*a*) Cadmium from zinc;
(*b*) Cadmium from magnesium;
(*c*) Zinc from magnesium;
(*d*) Cadmium from aluminum;
(*e*) Cadmium from silver?

Write equations.

20. What metals will be removed from metallic mercury by trickling it through a solution of mercurous nitrate? Illustrate by an equation.

21. Give equations for:

(*a*) Preparation of calomel by precipitation.
(*b*) Preparation of mercuric iodide by precipitation.
(*c*) Dissolving metallic mercury in hot concentrated sulfuric acid.
(*d*) Reduction of corrosive sublimate to calomel, by metallic mercury.
(*e*) Decomposition of mercuric nitrate by heat.

22. What connection is there between the ready hydrolysis of mercury salts and the fact that no carbonate of mercury has ever been prepared?

23. What compound is precipitated on adding sodium carbonate to a solution of mercuric chloride. Write equation.

24. Whenever a chemical substance exists in two different forms, the unstable one is the more volatile and the more soluble of the two. Apply this principle to explain the conversion of black mercuric sulfide into the stable red form by sublimation or by warming with an alkali sulfide.

25. Calomel is made commercially by subliming a mixture of mercuric sulfate, mercury, and common salt. Write the equation involved.

26. With the help of the replacement series, explain the destruction of lead plumbing by solutions of mercury salts.

27. Describe remedial measures to be taken in case of poisoning in the laboratory by chlorine, arsenic, mercury, cyanogen, hydrogen sulfide.

28. Mercurous sulfate (a slightly soluble salt) is made by electrolyzing dilute sulfuric acid, with a platinum cathode and a mercury anode. Write electronic equations to represent the changes at the two electrodes.

29. In the preceding problem, calculate the weight of mercurous sulfate formed in one hour by a current of 1 ampere (§ 425).

CHAPTER XLIV

TIN AND LEAD

Carbon and silicon, at the head of Group IV A in the periodic table, are typical non-metals. Germanium, next lower down, is still predominantly a non-metal, with some faint indication of metallic properties. Tin is on the border line between metals and non-metals; for its oxides dissolve in acids to form true tin salts (nitrate, sulfate, acetate, etc.), as well as in alkalies to form stannites and stannates (§ 569) in which tin forms part of a non-metallic radical. Lead behaves in much the same way, but is predominantly metallic.

TIN

565. Occurrence.—Tin generally occurs as **cassiterite or tinstone** (stannic oxide, SnO_2). It is an unusually heavy mineral, having a density (7.0) almost equal to that of metallic iron. It occurs in alluvial sands, in many parts of the world, as rounded lumps, colored brown or black by oxides of iron; and occasionally in veins in association with tungstates and various metallic sulfides.

The world now produces and consumes above 100,000 tons of metallic tin each year. About two-thirds of this now comes from the Dutch East Indies and the neighboring Straits Settlements—a British colony at the tip of the long peninsula that reaches down into tropical waters from the southeastern extremity of the Asiatic continent. Chinese coolies are there employed by the hundred thousand, working over the alluvial sands, by primitive methods that in most other parts of the world have long since been supplanted by the steam shovel and centrifugal pump.

Bolivia produces about a fifth of the world's supply of tin, from mines situated at altitudes exceeding those of any of the peaks of the Rocky Mountains or Alps. Tasmania, just south of Australia, is another important source, as is Cornwall, on the southern coast of England.

The United States, which leads the world in the production of petroleum, coal, iron, copper, aluminum, silver, zinc, mercury, and lead, produces practically no tin at all. Yet there are other metals that could be substituted for tin in most of its applications. In case of need our demand could probably be reduced very considerably.

566. Metallurgy of Tin.—Metallic tin is prepared by a very simple metallurgical process: (1) The ore is crushed and given a preliminary concentration by washing with water. (2) It is then roasted to remove sulfur and arsenic and passed through a magnetic separator to free it from magnetic iron oxide. (3) The purified material, now consisting largely of stannic oxide, is reduced by coal in a reverberatory furnace or small blast furnace. The process is chemically very much like that used for the production of zinc (§ 551); but tin, though it melts at about the same temperature as zinc, is much less volatile. It is therefore tapped off at the bottom of the furnace in liquid form, instead of distilling off as vapor.

It is necessary to refine the tin thus obtained, by reheating on a sloping hearth with a sufficient supply of air to remove some of the more readily oxidizable elements, such as zinc and lead. The purified metal is drained away and cast into bars (**block tin**); and the impure residue, or dross, resmelted with a fresh supply of ore.

567. Properties and Uses of Metallic Tin. Tin lies just above hydrogen in the electrochemical series. It decomposes water vapor at temperatures above its melting point, forming tin dioxide, and liberating hydrogen; but at room temperature the action is imperceptible. Metallic tin may be exposed to moist air for years, without tarnishing in the least.

Most of the uses of metallic tin depend on this **non-tarnishing quality,** on the fact that it **may be rolled out into thin sheets** at the temperature of boiling water, and on its **low melting-point.** (1) Tin cans are made from tin-plate, i.e., sheet steel which has been carefully cleaned, and dipped into molten tin. (2) Enormous quantities are used in the form of tin-foil for wrapping chewing-gum and confectionery. (3) Block tin is used in the chemical laboratory for condenser tubing, in work requiring distilled water of unusual purity. Steam condensed in tubes of ordinary soft glass, in absence of CO_2, commonly dissolves enough alkali to color phenolphthalein. (4) Most low-melting alloys contain tin.

Solder is an alloy of about equal parts tin and lead. This adheres to metallic surfaces better than pure lead, for it oxidizes less readily. Tin alone would serve, but would be needlessly expensive.

Babbitt metal is tin, alloyed with a few per cent of antimony and copper. It retains a smooth surface when worn, and accordingly is used as a bearing metal, to retain the ends of rotating shafts.

Bronze is an alloy of tin and copper (§ 532). For the uses of tin compounds, see § 570.

568. Allotropic Forms of Tin.—Considerable practical interest attaches to the fact that the **common (tetragonal) form of tin,** capable of being rolled into sheets, is stable only within the temperature range 18° to 170° C. Below 18° C. it may go over into a brittle allotropic form called **gray tin,** the transformation being the more rapid the lower the temperature. Thus, in very cold weather, tin roofs and organ pipes have frequently crumbled to powder. Moreover, at temperatures above 170° C., **rhombic tin,** a third allotropic form, is produced. This is brittle enough to be powdered in a mortar.

$$\begin{array}{ccccc} & 18^\circ\text{ C.} & & 170^\circ\text{ C.} & \\ \text{Gray tin} & \rightleftarrows & \text{Tetragonal tin} & \rightleftarrows & \text{Rhombic tin.} \\ & & \text{(Malleable)} & & \\ \text{Sp. g. } 5.8 & & 6.55 & & 7.25 \end{array}$$

The possibility of making industrial use of metallic tin is thus seen to depend on the existence of a malleable allotropic form having a rather limited temperature range of stability, that fortunately happens to include room temperature. Not only tin, but most other heavy metals are believed to exist in two or more allotropic forms, the case of iron (§ 499) being a particularly interesting and important one. Among the non-metals we have noticed a similar behavior on the part of sulfur (§ 226), phosphorus (§ 310), and carbon (§§ 329, 330).

569. The Stannous and Stannic Compounds.—Tin forms two oxides and two series of salts, in which its valence is respectively two and four. The lower stage of oxidation (***valence two***) is represented by stannous oxide (SnO), stannous salts (as $SnCl_2$), and the stannites (as Na_2SnO_2).

The white precipitate called **stannous hydroxide,** arbitrarily (§ 471) represented by $Sn(OH)_2$, is prepared by precipitating any stannous salt with an alkali or an alkali carbonate:

$$SnCl_2+Na_2CO_3+H_2O=Sn(OH)_2+2NaCl+CO_2.$$

Stannous oxide and hydroxide are **amphoteric** (§ 473); thus they dissolve in acids to form stannous salts,

$$Sn(OH)_2+2HCl=\underset{\substack{\text{Stannous}\\\text{chloride}}}{SnCl_2}+2HOH;$$

and in alkalies (except NH_4OH) to form alkali stannites,

$$Sn(OH)_2+2NaOH=\underset{\substack{\text{Sodium}\\\text{stannite}}}{Na_2SnO_2}+2HOH.$$

Stannous salts are produced when metallic tin is dissolved in dilute, non-oxidizing acids, in the absence of air.

Both the stannous salts and the stannites are **powerful reducing agents.** Thus, stannous chloride will easily reduce mercuric chloride to mercurous chloride or metallic mercury, being itself oxidized to the stannic condition (§ 564); while sodium stannite will reduce bismuth hydroxide to metallic bismuth, being itself oxidized to sodium stannate.

Write molecular and ionic equations for these three reactions. They serve as analytical tests for mercury and bismuth, and hence, conversely, for tin.

The higher stage of oxidation of tin (valence **four**) is represented by stannic oxide (SnO_2), stannic salts ($SnCl_4$), and the stannates (Na_2SnO_3).

Stannic hydroxide is prepared by precipitating a stannic salt with an alkali or alkali carbonate. Dried in the air, this is a white powder approximating the composition $Sn(OH)_4$. Since it combines readily with bases to form salts, stannic hydroxide is often termed **orthostannic acid,** and written H_4SnO_4. Dried over sulfuric acid it loses water and becomes **metastannic acid,** H_2SnO_3.

Another form of metastannic acid, which differs from the precipitated material in being practically insoluble in acids and alkalies, is prepared by oxidizing metallic tin or tin compounds with concentrated nitric acid.

Write and balance equation for the oxidation of metallic tin with concentrated nitric acid.

Stannic chloride, $SnCl_4$, is a liquid prepared by treating metallic tin with an excess of chlorine. The process is used commercially in recovering tin from tin scrap.

570. Technical Uses of the Compounds of Tin.—The chief uses of metallic tin have already been given (§ 567). The most important compounds are SnO_2, $SnCl_2$, and $SnCl_4$.

1. **Stannic oxide, SnO_2,** is conveniently produced by igniting metastannic acid, prepared by either of the methods just described. It is a white powder, of the same composition as cassiterite. It is a constituent of nearly all the brilliant white enamels applied to enameled kitchenware and enameled earthenware.

2. **Stannous chloride, $SnCl_2 \cdot 2H_2O$,** is prepared by dissolving metallic tin in hydrochloric acid, and evaporating the solution.

It is used as a mordant in dyeing (§ 372), being readily hydrolyzed, and depositing $Sn(OH)_2$ within the fibers. A solution of stannous chloride is an important laboratory reducing agent, which must be made strongly acid with HCl to prevent hydrolysis, and kept in contact with metallic tin to prevent oxidation.

3. **Stannic chloride, $SnCl_4$,** is a colorless fuming liquid, prepared by action of an excess of chlorine on metallic tin (detinning tin scrap), or on stannous chloride. This, like stannous chloride, is used as a mordant. It dissolves in alkalies to form metastannates:

$$SnCl_4+6NaOH=\underset{\substack{\text{Sodium}\\\text{Metastannate}}}{Na_2SnO_3}+4NaCl+3H_2O.$$

Give an ionic formulation of this reaction.

Sodium metastannate is used in fireproofing cotton and linen goods. The cloth is soaked in a strong solution, then dipped in $(NH_4)_2SO_4$. The ammonium metastannate formed is hydrolyzed and metastannic acid deposited in the fiber.

571. Analytical Tests for Tin.—1. Tin is precipitated by hydrogen sulfide from acid solutions, as stannous sulfide, SnS, or stannic sulfide, SnS_2, without change of valence:

$$SnCl_2+H_2S=\underset{\text{Brown}}{SnS}\downarrow+2HCl,$$

$$SnCl_4+2H_2S=\underset{\text{Yellow}}{SnS_2}\downarrow+4HCl.$$

2. Tin cannot be distinguished from arsenic by the preceding test, for both the sulfides of arsenic are yellow, and, like SnS_2, dissolve in yellow ammonium sulfide solution. But there are several specific tests for arsenic (§ 319); and tin, in the stannous condition, may be identified by its reducing properties, and in particular by its reactions with mercuric chloride and bismuth hydroxide (§ 569).

LEAD

572. Occurrence.—The principal ore of lead is **galena** or lead sulfide, PbS, which is found in large cubical crystals, of a bluish-black hue, quite similar to that of the pure metal. Deposits of the sulfate, carbonate and chromate of lead are of less importance and are commonly found in the neighborhood of veins of galena, from which they appear to have been formed by gradual alteration.

The world's production of metallic lead has recently been over a million tons in a single year—about the same as that of copper or zinc, and second only to the production of iron and steel. The United States produces about half of the total, and Canada about a third; while Mexico, Japan, Great Britain, and Central Europe furnish noteworthy amounts.

573. Metallurgy of Lead.—There are so many different methods for the extraction of lead from its ores that any detailed examination of the subject would fill an entire volume. Of the processes now in use, we shall outline three of the most important:

(1) The first of these may be employed **whenever a lead sulfide ore is reasonably free from other sulfides, provided silica is also almost absent,** or has been removed by concentration. The ore is first roasted at a low temperature in a reverberatory furnace in the presence of a limited supply of air. By this means a part of the PbS is oxidized to PbO and $PbSO_4$. The temperature of the furnace is then raised, when the unchanged lead sulfide serves as a reducing agent to reduce the oxidized compounds to metal:

$$PbS+2PbO=3Pb+SO_2;$$
$$PbS+PbSO_4=2Pb+2SO_2.$$

(2) In the United States, at least, it is frequently found necessary to "**sweet roast**" or "**dead roast**" the ore, i.e., **to oxidize and remove the sulfur and arsenic completely.** A certain part of the lead oxide thus produced unavoidably reacts with the silica to form a lead silicate.

$$2PbS+3O_2=2PbO+2SO_2;$$
$$PbO+SiO_2=PbSiO_3.$$

The completely roasted material is then charged into a small cylindrical furnace and reduced at a low red heat by powdered **coke:**

$$PbSiO_3+C=Pb+CO\uparrow+SiO_2;$$
$$SiO_2+CaO=CaSiO_3.$$

(3) In an interesting process, occasionally found useful **with** highly silicious ores, **galena is reduced directly with iron:**

$$PbS+Fe=Pb+FeS.$$

574. Lead Refining.—The crude lead produced by the preceding methods always carries a quantity of silver that is worth recovering. Moreover, it contains small amounts of antimony, copper, iron, and other metals, which render it hard and brittle. The silver is removed as described in § 540, item 2. The desilverized lead is cast into anodes, which are suspended in a solution of lead fluosilicate, $PbSiF_6$, and electrolyzed (Betts process) in the presence of a little gelatin. The deposit of lead thus obtained, on sheets of previously refined material, is almost perfectly pure; since the various foreign metals either form insoluble fluosilicates, and are precipitated; or else stand higher in the electrochemical series than lead itself, and thus of necessity remain behind in the electrolyte while the lead is being deposited (§§ 422, 531).

575. Properties of Metallic Lead.—Lead is a soft, gray metal, of **low melting point** and **very slight tensile strength.** When heated near its melting point it becomes soft as butter, and may be pressed through a ring-shaped opening, to form pipe. The same property enables the plumber to connect lengths of lead pipe by "wiping" the joint with a rag covered with the softened metal.

Lead oxidizes slowly in the air, but soon becomes covered with a dull gray coating of basic carbonate, which protects it from further corrosion. It is slowly dissolved by most dilute acids, forming soluble lead salts, and liberating hydrogen. Even carbonic acid will dissolve lead slowly; hence lead pipes may safely be used for drinking water only in case the water is found to deposit a coating or scale over the interior surface of the pipe.

Lead is **but slowly attacked by dilute sulfuric acid,** presumably because lead sulfate is an insoluble substance, and tends to coat over and protect the surface exposed to the action of the acid.

576. Uses of Metallic Lead.—In addition to its use in plumbing and for lining acid chambers, metallic lead is sometimes used as a substitute for zinc and tin, for protecting the surface of sheet steel. A number of other uses are suggested in the diagram below. Decorative windows, for example, are composed of bits of colored glass separated and held in place by lead ribbon.

Lead forms a number of useful alloys. Its use in **solder** (§ 567) **and fuses** (§ 558) has previously been mentioned. **Type-metal** contains as much as 25 per cent antimony, which gives increased hardness and causes the alloy to expand in solidifying, thus producing a casting with well-defined edges. Lead alloyed with about $\frac{1}{2}$ per cent arsenic has extraordinary hardness, and is used for shot.

LEAD ORE

Pig Lead

Sublimed White Lead **Sublimed Blue Lead**	**Litharge** **Red Lead**	**Lead Carbonate**	**Metallic Lead**
Rubber tires	Storage batteries	Mixed paints	Telephone cable
Oil cloth	Optical glass	Wallpaper	Sulfuric acid plants
Shade cloth	Oil refining	Coated paper	Babbitt metal
Linoleum	Rubber	Enameled ware	Type-metal
Metal paints	Greases	Chinaware	Electric fuses
	Varnish driers	Printing inks	Lead foil
	Metal paints	Dyes	Lead pipe
	Pipe fittings	Lead acetate	Church windows
	Insecticides	Lead nitrate	Tubing for player pianos
	Safety matches		Sash weights
	Enamels		Solder
	Lead glazes		
	PbO-glycerol cement		Storage batteries

577. Litharge.—**Litharge,** or **lead monoxide, PbO,** is **the most stable and the most important of the several oxides of lead.** It is a heavy yellow or orange-yellow powder, often distinctly crystalline. It is produced by **cupellation** (i.e., oxidation in a current of air) of lead or lead-silver alloy.

The most important uses of litharge are indicated in the preceding diagram. We have already described applications in refining petroleum (§ 343), and in preparing optical glass (§ 407), enamels and glazes, varnish-driers and vulcanized rubber (§ 353). Mixed with glycerol, litharge forms a thick paste, hardening in a few hours, **useful for cementing stone and glass.**

Litharge is slightly soluble in water, and its solution is **distinctly alkaline;** but in spite of this definitely basic character, it shows

feeble acid traits, in so far as it is able to dissolve in alkalies to form **plumbites** (analogous to the stannites, § 569):

$$PbO+2NaOH=Na_2PbO_2+H_2O.$$

Give an ionic formulation of this reaction.

578. Red Lead and Lead Dioxide.—When litharge is heated for a long time at a temperature of about 500° C., it unites with a further quantity of oxygen, and is transformed into a bright red powder, Pb_3O_4, called red lead, or **minium.** This has the general properties and uses of litharge itself, but is, in addition, an oxidizing agent. Thus, when minium is mixed with linseed oil, the latter is oxidized and hardened (§ 362)—a property which is applied in caulking joints in steam- and gas-pipes.

Lead peroxide (better called lead dioxide) is a brownish-black powder prepared (1) **from red lead** by electrolytic oxidation or by extraction with dilute HNO_3:

$$Pb_3O_4+4HNO_3=2Pb(NO_3)_2+PbO_2+2H_2O;$$

or (2) **by oxidizing a solution of litharge in NaOH,** i.e., sodium plumbite (§ 577), with bleaching powder or chlorine:

$$Na_2PbO_2+CaOCl_2+H_2O=2NaOH+CaCl_2+PbO_2.$$

Lead dioxide is a vigorous oxidizing agent, as is witnessed by the fact that it will cause a stream of hydrogen sulfide to ignite spontaneously. Its chief use is in storage cells (§ 579). It dissolves somewhat in alkalies, forming plumbate solutions:

$$PbO_2+2NaOH=\underset{\substack{\text{Sodium}\\\text{plumbate}}}{Na_2PbO_3}+H_2O.$$

579. The Lead Storage Cell.—The storage cell, or **accumulator,** contrary to the popular opinion, does not store up electricity, but chemical energy, which may be converted into electrical energy at will. The most common and successful of such cells has a plate of **spongy lead,** and one of **lead dioxide,** dipping into a solution of sulfuric acid (about 30 per cent H_2SO_4 by weight). **During discharge both electrodes become covered with a deposit of lead sulfate;** but, when a current is sent through the cell in the opposite direction, the reactions at the electrodes are reversed, and the plates restored to their original condition.

Lead plate $$\underset{\text{Cathode}}{\overset{\text{Anode}}{Pb}} + SO_4^{--} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4 \text{ (solid)} + 2e$$

Dioxide plate $$\underset{\text{Anode}}{\overset{\text{Cathode}}{PbO_2}} + SO_4^{--} + 4H^+ + 2e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4 \text{ (solid)} + 2H_2O$$

The direction of the current through the cell, when charging or discharging, may be found by recalling that the plate which is being oxidized always serves as anode, and that which is being reduced as cathode (§ 424). Thus, during discharge, the lead plate is oxidized from Pb to $PbSO_4$ (valence increased from 0 to 2). In this process the lead plate therefore serves as *anode*, or is the plate at which the electrons *enter* the outer circuit or, at which the " current " *leaves* the outer circuit (§ 424).

The reactions at the surface of the lead dioxide plate are doubtless accomplished in several steps, but opinions differ concerning the details. The electromotive force of a fully charged cell is a little over 2.0 volts, and decreases slowly during discharge. When it has fallen to about 1.8 volts, it should be recharged.

580. White Lead.—When a solution of a soluble lead salt is precipitated with ammonium carbonate, a finely divided, white precipitate is produced, **normal lead carbonate,** $PbCO_3$. When this is stirred up with lead hydroxide, in the presence of a little water, a reaction takes place which results in a hardened mass of **basic lead carbonate,** approximately $Pb(OH)_2 \cdot 2PbCO_3$ (compare with § 449).

Basic lead carbonate is an important paint pigment, commonly known as **white lead.** It is sometimes made from precipitated lead carbonate, as just described; but **the usual method is to expose granulated lead or perforated lead plates, for a period of a week or more, to the action of steam, carbon dioxide, and acetic acid vapor.**

This is an elaboration of the famous Dutch process, many centuries old, in which the heat and carbon dioxide were supplied by fermenting manure or tan-bark. The acetic acid vapor, in the presence of air, acts on the lead to form basic lead acetate, which is then precipitated by the carbon dioxide.

Sublimed white lead is made by roasting a plumbiferous zinc ore (i.e., ZnS and PbS) in a current of air, and consists of a mixture of zinc oxide and basic lead sulfate. It is said to have all the virtues of the blended white pigments containing zinc oxide and ordinary white lead (§ 554).

581. Other Commercially Important Lead Compounds.—When litharge or lead carbonate is dissolved in acetic acid, lead acetate is obtained, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$. This salt has a sweet taste (whence the unfortunate name, **sugar of lead**), but is highly poisonous, like all other lead compounds. It is sometimes used as a mordant in dyeing cotton cloth.

When litharge is boiled with a solution of lead acetate it gradually dissolves, forming a mixture of *basic lead acetates*, for example $Pb(OH)(C_2H_3O_2)$. This is sometimes used in the manufacture of white lead.

Lead arsenate (§ 320) is a constituent of sprays for controlling leaf-devouring insects. *Lead chromate* is an important yellow pigment.

582. Analytical Tests for Lead.—Any compound or mineral containing lead may be readily recognized by mixing it with a little sodium carbonate, and heating it with a blowpipe in a depression in a stick of charcoal. A bead of metallic lead is formed, surrounded by a ring of litharge, red when hot, and yellow when cold.

Lead in solution (i.e., lead-ion) may be detected by a number of simple tests:

(1) H_2S gives a **black precipitate, PbS,** even in the presence of active acids. The precipitate dissolves in boiling dilute HNO_3 (distinction from HgS).

(2) H_2SO_4 or any soluble sulfate gives a finely crystalline **white precipitate of $PbSO_4$.**

(3) Soluble iodides precipitate **yellow PbI_2,** soluble in boiling water or in excess of KI (compare with HgI_2, § 562).

(4) Soluble chromates and dichromates precipitate **yellow $PbCrO_4$:**

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4\downarrow + 2KNO_3 + 2HNO_3.$$

Give an ionic formulation of this reaction.

EXERCISES

1. Write equation for a practical method for recovering tin from tin cans.

2. Write and balance molecular equations for the reactions that take place when metallic tin is boiled with solutions of each of the following:
HCl, $HC_2H_3O_2$, HNO_3, NaOH, $CuCl_2$, $FeCl_3$, $AlCl_3$, $HgCl_2$, $SnCl_4$. There is a reaction in each case.

3. Write the preceding equations in ionic form.

4. Give equations to explain why stannous carbonate cannot be prepared by double decomposition in solution.

5. Give equations to explain the use of the metastannates in fireproofing cloth.

6. Starting with cassiterite, describe methods for preparing metallic tin on a laboratory scale; then, in succession, stannous chloride, stannous hydroxide, sodium metastannite.

7. Write and balance equations for the reactions that take place when each of the following, first in equivalent amount, then in excess, is added to a solution of stannous chloride:

$$NH_4OH, NaOH, Na_2CO_3, H_2S.$$

8. What are the principal ions present in solutions of stannous chloride and sodium stannite respectively? Toward which electrode is the tin transported, in each case, when a current is passed?

9. Write equations for the roasting of galena in a limited supply of air.

10. Write equations for the reactions taking place when metallic lead is boiled with dilute solutions of each of the following:

HNO_3, $HC_2H_3O_2$, $NaOH$, $FeCl_3$, $AgNO_3$, H_2SO_4, $NaHCO_3$.

11. What is meant by each of the following:

Cupellation, roasting, basic salt, minium, plumbiferous ore, sublimed white lead, sugar of lead?

12. Write equations to show what happens when litharge is boiled with solutions of each of the following:

Nitric acid, acetic acid, lead acetate, bleaching powder, sodium carbonate, sodium hydroxide, sodium sulfide.

13. Sheet lead is sometimes used for lining the wooden crystallizing tanks used in the commercial preparation of copper sulfate (§ 538). What property of lead sulfate makes this possible? Why would not sheet copper serve? Sheet iron or sheet zinc?

14. Write equations for the successive reactions in the preparation of white lead from metallic lead.

15. White lead has sometimes been prepared by electrolysis of a solution of sodium carbonate and sodium chlorate, with lead electrodes. Is the anode or cathode corroded (§ 426)? Assuming lead chlorate to be first produced, give formulations of the reactions taking place at the electrodes.

16. When a stick of zinc is hung in a solution of lead acetate, it becomes coated with branching crystals, forming a " lead tree." Explain.

17. Write equations for the preparation of lead arsenate and lead chromate in several successive steps, starting from litharge, arsenic trioxide, and chromic chloride.

CHAPTER XLV

THE ELEMENTS OF MINOR INDUSTRIAL IMPORTANCE

Thirty-five elements have been considered in the preceding pages—barely more than a third of the total number known. Yet these thirty-five represent all the different natural groups of elements, and permit us to forecast the behavior of those that have been reserved for the present chapter. The reasons for thus examining a few of the elements with great care, while giving all the rest a mere passing glance, are purely practical ones. It was felt that the student taking chemistry merely as a part of a general education would carry away a better understanding of the spirit of the science and the nature of its manifold contributions to human welfare, were he permitted to concentrate on a few important representatives of the more than eighty elemental types of matter.

The student who purposes specializing in chemistry, however, should learn something of the properties of the less familiar elements. The fact that they are of minor industrial value to-day signifies nothing. For some of them are not so very rare, and, when we have acquired a more thorough knowledge of their properties, may become of great importance. Titanium, for example, is more abundant than zinc, lead, copper, or any other heavy metal save iron, and aluminum; it finds many useful applications quite unknown a very few years ago.

Group 0
He
4.00
Ne
20.2
A
39.9
Kr
82.92
Xe
130.2
Rn
222.4

583. The Inert Gases.—The inert (or noble) gases are distinguished from all other elements by the fact that they form **no chemical compounds whatever.** They differ, furthermore, from the commoner gases, and resemble **metallic vapors** (Hg, Zn) in having but a single atom in the molecule.

Helium, the lightest of the inert gases (at. wt. = mol. wt. = 4.00) was discovered, by means of the spectroscope, in the atmosphere of the sun, many years before it was found on earth. It occurs in cavities in some rare minerals and in a few mineral springs; but its most important source is the natural gas wells of Kansas and Texas, which contain up to 2 per cent of the element. The one successful Government plant erected for the production of helium, for filling dirigible ballons, condenses the more volatile constituents of the natural gas in liquid-air machines (§ 54), and then by fractional distillation separates the helium from the liquid obtained. Helium is the only gas which is light enough to compete with hydrogen in buoyant effect, and has the inestimable advantage of being completely non-combustible.

Neon is contained in traces (§ 280) in the less readily condensable portions of the atmosphere. Its presence there may be shown by admitting a little air into an evacuated tube, containing a pair of platinum electrodes, and a little freshly ignited wood charcoal in a side-limb cooled to −185° C. All the other gases of the atmosphere are at once adsorbed by the charcoal (§ 327); and, on passing a discharge, one obtains the spectral lines of helium and neon. An electric current passed through rarefied neon gives a fine orange-red light, which has been used successfully in illumination, in mercury vapor lamps, to counterbalance the disagreeable greenish hue that is produced by the incandescent mercury vapor alone. Spark-plug testers depend on the same principle.

Argon resembles nitrogen very closely in boiling point and other physical properties, but is distinguished chemically by its failure to combine with other elements. Thus, when air is passed repeatedly over heated magnesium, the nitrogen and oxygen all combine with that element, leaving behind argon, with smaller quantities of other inert gases. Remarkably enough argon remained undiscovered until 1893, that is, for more than a century after the rise of modern chemistry, in spite of the fact that it makes up over 1 per cent of our atmosphere. At the present time, argon is used only for filling incandescent light bulbs.

Krypton and **xenon** occur only in very small quantities in the atmosphere. Thus, if the molecules of ordinary air were to file past an observer at the rate of one each second, he would see an argon molecule once every two minutes, on the average; but a krypton molecule only once in about eight months, and a xenon molecule once in five or six years.

Niton, or radium emanation, recently renamed **radon,** is formed by disintegration of radium, the other product being helium (§ 586). Radon has all the common properties of the other heavier members of the zero group (complete chemical inertness, condensation by liquid air), but is unstable, its atoms decomposing, with the formation of helium and radium-A. In consequence of this activity, radon glows faintly in the dark. Most remarkable is the fact that a rather complete study has been made of the properties of radon, including the determination of its boiling point, density, and rate of decomposition to form radium-A, in spite of the fact that there are no more than a few hundredths of a cubic millimeter available for study at any one time.

Group IA
Li
6.94
Na
23.00
K
39.10
Rb
85.45
Cs
132.81

584. The Rarer Alkali Metals.—**Lithium** occurs in nature as a lithium mica (§ 402), and to a smaller extent as a phosphate or alumino-fluoride. Lithium chloride, LiCl, is a very deliquescent salt, used in aluminum soldering. Lithium may be distinguished from sodium and potassium by the brilliant carmine color which it gives to the Bunsen flame, and by the fact that its phosphate and carbonate are nearly insoluble in water.

Rubidium and **cesium** are very rare elements found in mineral springs, and occasionally in mica in association with lithium. Like potassium, these two elements can be precipitated with chlorplatinic acid, giving yellow crystalline precipitates, Rb_2PtCl_6, Cs_2PtCl_6.

Group IIA
Gl
9.1
Mg
24.32
Ca
40.07
Sr
87.63
Ba
137.37
Ra
226.0

585. Beryllium.—Beryllium (often called glucinum) occurs in nature as beryl, a glucinum-aluminum metasilicate, $3GlO \cdot Al_2O_3 \cdot 6SiO_2$. This is often colored green by traces of chromium, and is then known as **emerald.** Metallic glucinum is prepared by electrolysis of fused glucinum fluoride, BeF_2, containing a little sodium fluoride to lower the melting point. It is a metal of silvery luster, and fails to decompose in water at any temperature below 100°; but, like aluminium, it dissolves easily in NaOH, forming glucinates, such as Na_2BeO_2.

Beryllium has the valence two in all its compounds.

But, though beryllium salts are accordingly like those of magnesium, so far as formula goes, in their properties they more strongly resemble those of trivalent aluminum, in the next column of the periodic table. Thus, beryllium is precipitated by ammonium hydroxide solution as the gelatinous hydroxide, $Be(OH)_2$, which remains undissolved in the presence of an excess of the reagent; while sodium hydroxide first precipitates the hydroxide and then redissolves it to form the glucinate, Na_2BeO_2. Compare § 480.

Beryllium hydroxide differs from aluminum hydroxide in being soluble in ammonium carbonate solution, and in being precipitated from solution in sodium hydroxide by long boiling. These properties are commonly applied in the separation of beryllium from aluminum.

586. Radium.—Many of the properties of radium and its salts are those that might be expected from its position in the periodic table. Thus, radium itself resembles barium, which occupies the space just above it, in Group II*A*, in being a silvery white metal (M. P. 700° C.), which tarnishes in the air, and acts on water to liberate hydrogen. Its volatile salts, like those of barium, give characteristic spectral bands in the flame. Radium sulfate, and radium carbonate, like the corresponding salts of calcium, strontium, and barium, are insoluble in water.

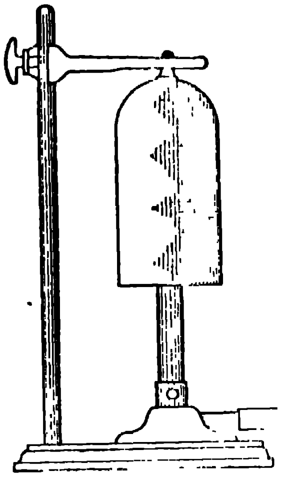


Fig. 128.—Testing a gas-mantle Maximum brightness is obtained if the mantle contains about 99 per cent ThO_2, and 1 per cent CeO_2.

In some other respects, however, the properties of radium are most unusual. All radium salts, and the metal itself, are **radioactive.** By this we mean that **they continuously emit energy,** in the form of heat, light, and invisible radiations. These radiations are able to penetrate sheets of paper, and some of them may even pass through thick blocks of lead (§ 601). **They affect a photographic plate, and *ionize air,* or render it a conductor of electricity.** Thus, if the gold leaves of an electroscope are caused to diverge by a stick of charged sealing wax, a sample of radium salt placed near the knob of the instrument will cause the charge to leak away, and the leaves to fall together.

A study of these phenomena, following the discovery of radium by Madame Curie, in 1903, soon disclosed some important facts:

1. **The intensity of the phenomena of radioactivity**—measured, for example, by the rate at which an electroscope is discharged, when a sample of radium salt is brought into its neighborhood—**is proportional to the actual amount of radium present, but is independent of its state of combination.** A physician buying radium for the cure of cancer need not be concerned whether he receives the bromide, chloride, sulfate, or the uncombined metal. The thing that counts is the quantity of radium element present, whether free or combined.

2. **The intensity of the radioactivity, unlike other chemical phenomena, is not perceptibly affected by changes in temperature.**

A sample of radium emits energy at a definite, unchanging rate, whether it is plunged into liquid air, or heated in a furnace. Here is a phenomenon which man has learned much about, without discovering any means for its control.

3. **The intensity of the radioactivity continues for many years without perceptible diminution**, in apparent contradiction to the principle of conservation of energy, which states that no substance or combination of substances can continue to give off energy indefinitely, without deriving an equivalent supply of energy from some other source (§ 18).

This behavior of radium is a little like that of a man continuing to spend money, year after year without having any income. He could do this only if he possessed a considerable reserve capital. Thus, radium is now understood to be in possession of a considerable reserve supply of energy, stored up within its individual atoms, which it is gradually expending—consuming itself by slow degrees, like a bear in winter. But just as there is a limit to the life of a bear, subsisting by such means, so radium itself has a definite span of existence, a half of any given quantity disappearing within a space of about 1700 years. Its radioactivity, then—as measured by its ability to affect a photographic plate or discharge an electroscope—does decrease, after all; but at too slow a rate to be easily observable.

4. **The release of the store of energy within the radium atom does not proceed continuously, but by separate and successive disruptions of individual radium atoms**—just as the burden of water in a cloud is discharged by individual drops of rain. The fragments resulting from these repeated miniature explosions have been studied and identified, with the aid of the spectroscope, and in other ways. It turns out that **one of the products of the radioactive disintegration of radium is always helium,** a perfectly stable element. Other fragments, however, resemble the atoms of radium itself in being particles of ephemeral existence, coming to an end after a brief or a lengthy average life. The final products, after a number of generations of such elements, at the end of a long series of atomic catastrophes, are believed to be atoms of an isotope of lead. Details will be given in § 601.

587. Sources and Uses of Radium Salts.—Radium is always found in nature in association with uranium. Some ore is produced in Czechoslovakia and Australia; but the most important source of the two elements during recent years has been the **carnotite** deposits of Colorado and Utah. Carnotite is an impure potassium urano-vanadate ($K_2O \cdot 2UO_3 \cdot V_2O_3 \cdot 3H_2O$), which occurs as a cementing material, in sandstones. Commonly, such low-grade ore is used that about 150 tons are required for each gram of radium —a carload of ore for an amount of radium bromide that might be placed on the tip of a pen-knife. The price of radium has recently been materially reduced by the opening of new deposits of ore in the Congo. It is now about \$75,000 for 1 gram of the pure element. This means that a quantity of pure radium bromide, equal in weight to a postage stamp, may be purchased for about \$2000. In practice, radium salts are always put on the market in admixture with the corresponding salts of barium.

When radium is used in sufficient quantities, and with due regard to its dangerous qualities, it has proved of definite value in the cure of cancer. Since the total supply of the element is doubtless very small, it ought to be reserved for medical uses. A great deal has, nevertheless, been employed in luminous paints, for watch dials, and the like. These consist largely of a crystalline variety of zinc sulfide, with a trace of radium salt— though another radioactive element, mesothorium (§ 601), has recently often been substituted for the radium.

When one of the luminous spots on a watch dial is examined with a small lens, it is seen that what appears to the naked eye to be a steady glow consists, in reality, of a multitude of tiny, separate flashes. We can count the number of flashes occurring in a short interval of time, calculate the number that would occur in a period of several years, and then note how much helium gas comes into being during the same period, as a result of the decomposition of the radium. It has been found that the amount of helium is very nearly what we should expect, on the theory that each flash represents a miniature explosion, in which one atom of radium is completely disrupted, and an atom of helium produced. The helium atoms are hurled off with enormous velocities in the successive explosions, and each produces a flash of light, when it strikes against a crystal of zinc sulfide.

588. The Rare Earths.—Just below aluminum in the periodic table (§ 166) is a set of sixteen elements having very similar properties, known collectively as the **rare earth elements.** They resemble aluminum in having **a constant valence of three**—with the exception of cerium, which forms stable salts in valences three and four, and two others that form oxides of a higher valence (Pr, 5; Lu, 4).

The rare earths are easily distinguished from aluminum by the fact that their oxalates are insoluble in water. They are so much alike in their chemical properties that they are separated from each other with extreme difficulty. It is possible, however, to secure the different members of the group in reasonably pure form, and determine their individual spectra and atomic weights, by fractional crystallization (§ 97), or by methods based upon the fact that the rare earth elements of lowest atomic weight are most definitely electropositive (§ 414) in their behavior.

The rare earth elements are not at all rare in the sense of being hard to obtain for experimental study. In fact, enormous quantities of rare earth oxides are annually obtained as a by-product in the manufacture of thorium oxide for the preparation of gas-mantles (§ 593). The most important use of these rare earth oxides is in the production of **mixed metal,** which is an alloy of cerium with smaller amounts of the other rare earth elements. It is prepared by electrolyzing their fused chlorides, as has been described for calcium (§ 454). Mixed metal, and its alloys with iron and other heavy metals, produce sparks when struck. They are used in automatic gas-lighters.

Cerium fluoride is a constituent of the mixtures with which the cores of **flaming arc carbons** are filled. These are used as electrodes in the arc lamps employed in photo-engraving, and produce a light especially rich in chemically active (actinic) rays. The oxides of neodymium and praseodymium are sometimes used to impart a blue color to glass.

Group III	
A	*B*
B 10.9	
Al 27.1	
Sc 44.1	Ga 70.1
Yt 89.33	In 114.8
Rare Earths 139–179	Tl 204.0
Ac 230	

589. Gallium, Indium, and Thallium.—Distantly related to aluminum and the rare earth elements are the three metals gallium, indium, and thallium. These occur in minute quantities in zinc blende ores (§ 550). They all form salts in which the element has a valence of three, while indium also shows valences of one and two, and thallium of one. The basicity of these elements increases with increasing atomic weight. Thus, while gallium salts are easily hydrolyzed by water, those of indium are not. The thallic salts (valence three) are rather unstable, being decomposed on heating, with production of thallous salts (valence one). The three elements in this group at present have no commercial uses.

590. The Fourth Group of the Periodic System.—Group IV*A*, containing germanium, tin, and lead, and group IV*B*, containing titanium, zirconium, cerium, and thorium, are about equally related to C and Si.

Group IV

B		A
	C	
	12.005	
	Si	
	28.3	
Ti		Ge
48.1		72.5
Zr		Sn
90.6		118.7
(Ce)		Pb
140.25		207.2
Th		
232.15		

We have throughout a constant maximum valence of *four*, manifested in stable halogen salts and in oxides of the general formula MO_2. In group IV*A* we have, in addition, a valence of *two*, which is the usual valence in the case of lead. Because cerium has a constant valence of *three*, in addition to four, it has been described in the preceding section, along with the rare earth elements.

In this, as in most other groups, metallic properties increase with increasing atomic weight; though even tin and lead may be induced to enter a non-metallic radical (§§ 569, 577). Titanium and zirconium form stable salts in which the elements act as metals; but also titanates and zirconates, in which they act as non-metals. Thorium, at the bottom of the list is, as one might expect, exclusively metallic. It forms thoric salts (valence four), but no thorates.

591. Titanium.—Titanium occurs in small amounts in a great many minerals and soils. The total amount of it in the crust of the earth is accordingly very great. The principal titanium minerals are **rutile,** or titanium dioxide, TiO_2; and ferrous titanate, $FeTiO_3$.

Ferro-titanium alloys (ferro-carbon-titanium) are made by the reduction of iron-titanium ore with carbon in an electric arc furnace, very much as previously described for ferro-silicon (§ 410). If carbon must be absent in the finished alloy, a modification of the thermite process (§ 478) is employed. Aluminum is melted in an electric furnace, and reduces the powdered ore, then slowly added, to an alloy of iron and titanium:

$$4Al+3TiO_2=2Al_2O_3+3Ti.$$

The ferro-titanium alloys are used as scavengers (§ 496) in the manufacture of steel, since titanium combines readily both with nitrogen and oxygen. Titanium seems to be preferable to aluminum for this purpose, since the TiO_2 formed readily separates as a fusible slag; whereas Al_2O_3, being much more infusible, remains dispersed through the ingot, and may weaken the steel considerably.

Titanium dioxide, TiO_2, is a white powder prepared by igniting the precipitate formed when titanic salts are precipitated with sodium hydroxide. It has been used as a substitute for SnO_2 in enameled earthenware, and as a filler in oilcloth and rubber. A mixture consisting of about 25 per cent TiO_2, precipitated in the presence of 75 per cent $BaSO_4$, is an important white pigment.

The salts in which titanium has a valence of three are powerful **reducing agents.** Thus, titanous chloride, $TiCl_3$, is used as a bleach to discharge stains produced by colors that run in laundering. Other titanium salts are used for staining yellow and brown leather, and as mordants in dyeing wool.

592. Zirconium.—Zirconium occurs in nature as a silicate and as the oxide, ZrO_2, found in Brazil. The metal itself has been produced by the reduction of potassium zirconium fluoride, K_2ZrF_6, by metallic sodium or calcium. At present, the element is almost without commercial applications; but the oxide, sulfide, and silicate have been used to some extent as white pigments.

593. Thorium.—The principal thorium mineral is **monazite,** which is thorium phosphate, in association with the phosphates of cerium and the other rare earths. The chief deposit is in the monazite sands of the coast of Brazil, although North and South Carolina formerly produced considerable amounts.

The sand is first subjected to a magnetic separation, and is then digested with hot concentrated sulfuric acid The material thus decomposed is extracted with cold water, and a limited amount of magnesium oxide is added. Since thorium is more basic than cerium and the other rare earth elements, this treatment throws down thorium phosphate, $Th_3(PO_4)_4$, while leaving phosphates of the other elements in solution. From this precipitate, various thorium salts are prepared and purified by fractional crystallization.

All thorium salts are radioactive (§ 586).

Thorium oxide emits a brilliant white light when strongly heated; and, for reasons not yet understood, a mixture of thorium oxide with 2 per cent of cerium oxide is about seven times more luminous still. This fact is applied in the manufacture of incandescent gas mantles (Fig. 128), of which about 300,000,000 are made each year. The mantles are woven of ramie fiber, and dipped into a mixture of thorium and cerium nitrates, with sufficient beryllium or magnesium nitrate to give body to the finished product. The ash that is left, after the organic matter is burnt off, retains the shape of the original woven fabric, and contains CeO_2 and ThO_2 in the proper proportions. A layer of pyroxylin (§ 370) is next applied, to lend the mantle sufficient mechanical strength to withstand transportation.

594. Germanium.—Germanium is found in a few rare sulfide minerals, and in zinc blende (§ 550). One of the most noteworthy things about it is the fact that its existence, and many of the chemical properties of its compounds, were predicted by Mendelejeff, on the basis of the periodic table, almost twenty years before its actual discovery (§ 170). It is a grayish-white element, with a metallic luster, but is typically non-metallic in most of its reactions. Thus the dioxide, GeO_2, dissolves in alkalies to form germanates, analogous to the stannates (§ 569); but fails to dissolve in acids. The two germanium sulfides, GeS and GeS_2, have properties analogous to those of the two sulfides of tin (§ 571).

595. The Fifth Group of the Periodic System.—In column V*B* of the periodic table, we have a group of four rare elements: vanadium, columbium, tantalum, and protoactinium. An isotope of the latter is a radioactive element called brevium (from its extremely brief life, § 601). The best known elements in this group are found to resemble arsenic, antimony, and bismuth, in the principal branch of the fourth group, in forming compounds in which they manifest the valences three and five. But valences of two and four are fairly regular also.

Group V

B	*A*
	N
	14.008
	P
	31.04
Vd	As
51.0	74.96
Cb	Sb
93.1	120.2
Ta	Bi
181.5	208.0
Pa	
234	

Vanadium oxide is obtained as a by-product in extracting radium from carnotite (§ 585). We have already noted its use in an alloy steel (§ 501).

Columbium (sometimes called **niobium**) occurs in association with tantalum. The metal is prepared by methods similar to those described below for tantalum and has similar properties, but is less ductile and malleable. At present there are no commercial uses for columbium or its salts.

Tantalum occurs in nature as tantalic oxide, Ta_2O_5, in association with ferrous and manganous oxide. This is purified by fusion with $KHSO_4$, dissolved in HF, and precipitated as potassium fluotantalate, K_2TaF_7. Metallic tantalum is prepared by electrolysis of fused potassium fluotantalate or an aqueous solution of ammonium tantalate. It has many of the valuable qualities of platinum: hardness, malleability, ductility, resistance to rust, and extremely high melting-point (2850° C., compared with 1750° C. for Pt). Before the introduction of drawn tungsten (§ 599) tantalum was much used for filaments for incandescent lights. It would be very serviceable for surgical instruments, but in such applications would have to compete with a much cheaper material, stellite (§ 520).

596. The Sixth Group of the Periodic System.—The two branches of Group VI are very distantly related to each other. The elements in both branches are indeed alike in forming oxides of the formulas RO_2 and RO_3,* which behave as acid anhydrides. But in the principal branch (VI*A*) selenium is completely non-metallic, and tellurium almost completely so; while in the sub-branch (VI*B*) chromium, molybdenum, tungsten, and uranium enter into non-metallic radicals to form chromates, molybdates, etc., but also form well-defined metallic salts.

Group VI

B	*A*
	O
	16
	S
	32.06
Cr	Se
52.0	79.2
Mo	Te
96.0	127.5
W	Po
184.0	210
U	
238.2	

597. Selenium and Tellurium.—Selenium and tellurium occur in small quantities in a great many sulfide ores. Their chief commercial source is thus the dust that accumulates in the flues of pyrite burners, in the manufacture of sulfuric acid (§ 240). **Tellurium** in addition occurs in association with gold, silver, lead, etc., as minerals of variable composition ("gold telluride," § 547).

Many of the properties of these two elements may be anticipated from their relationship to sulfur. **Selenium,** like sulfur, occurs in a number of different allotropic forms. The electrical conductivity of one of these forms is very much increased after exposure to light for a few seconds. Moderately successful attempts have been made to utilize this property in photo-electric cells, for reception of signals transmitted by a beam of light. Selenium, like sulfur, combines directly with many metals and non-metals, though the selenides thus produced are, in general, less stable than the sulfides. Selenium oxychloride, SeO_2Cl_2, promises to be a useful solvent for dissolving resins and other substances, insoluble in water and organic solvents. Elementary selenium is used in ruby-colored glass (§ 411). A very small percentage, in aluminum or copper, hardens these metals very considerably.

Tellurium has properties very similar to those of selenium, but shows faint indications of metallic properties, in that the dioxide, TeO_2, dissolves in nitric acid to form a nitrate $Te(NO_3)_4$.

598. Molybdenum.—Molybdenum occurs in nature chiefly as **lead molybdate,** $PbMoO_4$, and as molybdenum disulfide **(molybdenite),** MoS_2. The sulfide ore is roasted and extracted with sodium hydroxide, forming sodium molybdate, Na_2MoO_4. This solution is acidified with nitric acid, when molybdic acid, $H_2MoO_4 \cdot H_2O$, separates. This may be dehydrated by heating, to form **molybdic anhydride, or molybdenum trioxide,** MoO_3, a yellowish-white powder. This is purified, and reduced with hydrogen in an electric furnace, giving metallic molybdenum. The metal may also be prepared by the thermite process (§ 478).

Molybdenum is a silvery-white metal and is malleable and ductile when hot. It is used for the supporting wires over which the tungsten filaments are looped, within incandescent light bulbs. Its ductility and high melting-point (2500° C.) make it useful in winding small electric furnaces, which may be operated up to about 1600° C.; but at such high temperatures it needs to be protected very carefully against oxidation, by passing a stream of hydrogen through the jacket surrounding the winding of the furnace.

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* But $O \cdot O_3$ and SeO_3 are unknown.

Molybdenum is non-metallic in its chemical properties; for the lower oxides, M_2O_3 and MO_2, form no stable salts excepting halides. The oxide MoO_3 is the anhydride of molybdic acid, $H_2MoO_4 \cdot H_2O$, of which a number of salts are known. But many of the soluble molybdates are of a rather complex composition. **Ammonium molybdate,** for example, prepared by evaporation of a solution of molybdenum trioxide in ammonium hydroxide, approximates the composition $5(NH_4)_2MoO_4 \cdot 7MoO_3$. This is used as a reagent for the precipitation of phosphates (§ 315).

599. Tungsten.—Tungsten occurs as calcium tungstate (**scheelite**) $CaWO_4$, and ferrous-manganous tungstate (**wolframite**), $[Fe, Mn]WO_4$. By fusion of these minerals with sodium carbonate and extraction of the fused mass with water, it is possible to prepare sodium tungstate, $Na_2WO_4 \cdot 2H_2O$. Acids precipitate white tungstic acid, $H_2WO_4 \cdot H_2O$, from solutions of this salt. Tungstic acid loses water on being heated, giving **tungstic anhydride,** WO_3, which may be reduced to metal by heating in an electric furnace in a current of hydrogen, as described for molybdenum.

Metallic tungsten, thus produced, is a heavy gray powder, which is molded into bars by hydraulic pressure, then sintered in an electric furnace, and mechanically worked at a high temperature. The particles of the original metallic powder are thus very gradually elongated, until the bar, now become a slender rod, acquires a fibrous structure, and is very tough and strong. When it has been drawn down to very fine wire, it has a tensile strength equal to that of soft steel. Some of the filaments now produced for incandescent lamps have a diameter scarcely a fifth of that of a human hair (0.01 mm.).

Tungsten, like molybdenum, can be used for winding electric furnaces, for it has the highest melting-point of any of the metals (3540° C.). **Tungsten, like molybdenum, is non-metallic,** the lower oxide, WO_2, having no basic properties. Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, is used for fireproofing cotton goods.

600. Uranium.—The most important uranium mineral is **carnotite,** already mentioned as a source of radium (§ 587). Uranium oxide, obtained as a by-product in the extraction of radium, is used in the preparation of uranium glass. This has a greenish-yellow fluorescence, due to the lengthening of the wave length of a part of the invisible ultra-violet rays contained in ordinary white light. Uranium has been used occasionally in steel making, but is of no special importance.

Uranium forms a series of **uranous salts,** such as uranous sulfate, $U(SO_4)_2 \cdot 4H_2O$, in which it has a valence of four. But it also forms a series of basic salts, called **uranyl salts,** such as uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, in which it has a valence of six. These contain the uranyl group, UO_2, which plays the part of a bivalent metal.

The metallic conduct of uranium places it in rather sharp contrast to its relatives, molybdenum and tungsten, which are non-metallic in all their chemical properties.

The uranyl salts are yellow in color, and, unlike the uranous salts, possess a greenish fluorescence. The salts of both series, however, and metallic uranium itself, resemble the salts of radium and thorium in being **radioactive** (§ 586). Uranium is, in fact, an unstable element, decomposing slowly with the production of radium. This accounts for the fact that all uranium ores contain radium.

601. The Laws of Radioactive Change.—Review § 586. The peculiar properties possessed by the radioactive elements—their ability, for example, to affect a photographic plate wrapped in black paper, or to cause air to become a conductor of electricity, or to make certain minerals glow in the dark—was early found to be due to the fact that they emit invisible **rays** or **radiations.** These travel in straight lines, after the fashion of ordinary light, but are able to penetrate slight thicknesses of paper, wood, or even metal. As soon as a sample of a substance emitting these rays is placed in a magnetic field, it is observed that a part of the rays are deflected, or bent aside; some, indeed, to the left, but others to the right. This means that some of the rays carry positive electrical charges and others negative. A third type of rays, arising in many of the best-known cases of radioactivity, is quite unaffected by a magnetic field.

Alpha-rays.—The three types of rays differ in other important respects. The first type (the **alpha-rays**) are now known to consist of doubly positively charged helium atoms (He^{++}), sometimes called **alpha-particles.** These are hurled off from the radioactive material with such enormous velocities (around ten thousand miles a second) that molecules of air, with which they happen to collide, are *ionized*, or dissociated into electrically charged atoms. In consequence, the air becomes a conductor of electricity.

Beta-rays.—The second type of rays (the **beta-rays**) are shown to be negatively charged by the fact that they are deflected in the opposite direction from the alpha-rays, when placed in a magnetic field. Indeed they are now known to be streams of **electrons,** sometimes called **beta-particles,** moving in straight lines, with velocities of from about 16,000 to 180,000 miles a second. Since they are very light, the mass of an electron being not more than 1 1800th that of a hydrogen atom, they are very easily deflected by a magnetic field, and in very intense fields actually have their paths curled into spirals. These beta-rays are responsible for most of the photographic effect of radioactive substances.

Gamma-rays.—The third type of rays (the **gamma-rays**) being undeviated by a magnetic field, must be without electrical charges. They are, in fact, identical with X-rays, and appear to consist of vibrations in the ether, having a wave length perhaps a thousandth of that of ordinary light. The gamma-rays are remarkable for their penetrating power. In extreme instances they may pass through several inches of lead before being seriously weakened.

Summary of the Characteristics of the Three Types of Radiations.

	Alpha-rays. (α)	*Beta-rays.* (β)	*Gamma-rays.* (γ)
Nature	Doubly charged helium atoms	Electrons	Pulsations in ether.
Charge	+ +	—	None.
Deviation by mag. field	Slight	Very great	None.
Velocity	5% to 7.5% vel. of light	35% to 95% vel. of light	Vel. of light.
Range	Slight, but definite for any given radioactive substance	Generally greater, but not definite for any given radioactive substance	
Most conspicuous property	Ionizing effect	Photographic effect	Long range.
Fluorescent screens used	Zinc sulfide	Platinocyanides	Native zinc silicate (willemite).

Radioactivity and the Periodic Table.—Careful experiments have shown that the alpha- and beta-particles are not emitted simultaneously, but in succession. The unstable atom—that of uranium, let us say—goes to pieces in a series of successive "explosions," hurling off alpha- and beta-particles, one after another, like balls of fire from a Roman candle. Each of these explosions transforms the disintegrating atom into that of a new element; and within the past few years a great light has been thrown on the whole subject by the discovery that **the loss of an alpha-particle gives rise to a new element occupying a position two places to the left of the parent element in the Periodic table, and having an atomic weight four units less than that of the parent element.*** On the contrary, **the loss of a beta-particle gives rise to a new element one place to the right of the parent element, but not differing appreciably from it in atomic weight.**

Thus we have seen that radium is an element of Group IIA of the Periodic Table. When an atom of radium (at. wt. 226) goes to pieces, it always begins by losing an alpha-particle, being thus transformed into an atom of radon (at. wt. 222), an element of Group 0 (§ 583). But this fragment is apt not to exist very long before it too "explodes," losing another alpha-particle, and producing an atom of an isotope of polonium (at. wt. 218) in an element of Group VIA. A third alpha-particle is then ejected, leaving us with an atom of an isotope of lead (at. wt. 214), in Group IVA. Then follows the loss of a beta-particle, giving us an atom of an isotope of bismuth (at. wt. 214), in Group VA. Other changes follow, until we finally arrive at a stable element, which appears to be another isotope of lead.

The different radioactive elements have thus been recognized as belonging to three different "lines of descent." Radium, radon, and others trace their origin back to uranium. Still others are "descended" from actinium, itself very probably a product of the decomposition of uranium. The third series of elements is derived from thorium. Aside from these three groups of true radioactive elements, potassium and rubidium show feeble gamma-radiation, but none of the other phenomena of radioactivity.

The Law of Radioactive Decay.—The disintegration of the atoms of the radioactive elements follows what may be called the **reversed**

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* Since the atomic weight of helium is four.

compound interest law. A sum of money, placed at compound interest at any given rate, will double itself in a definite term of years; then in an equal period will double itself again. A radioactive substance on the other hand, gradually *disappears.* Half of any given sample passes out of existence in a definite period of time; and half of what remains in the next equal period. The **periods** of the different radioactive elements—the time, that is, in which half of any given sample will disappear—varies enormously. In the case of one of the isotopes of uranium (uranium I) it is about 13,000,000,000 years; others have periods of a few years, a few days, or a few seconds. The period of thorium C′ is less than a billionth of a second. Of course the rate of decomposition of the radioactive elements with very long or very short lives has not been determined directly, but is merely calculated from observations of the distance that the alpha-radiations are able to penetrate air. For it happens that the shorter the period of an element the more energetically its atoms hurl off alpha-particles when they " explode."

Emission of the Alpha-particles.—It is in connection with this emission of alpha-particles that some of the most beautiful experiments in the whole field of radioactivity have been performed. We have previously mentioned the fact (§ 586) that when a trace of a radium salt is in contact with a zinc sulfide screen, the alpha-particles, as they strike against the screen, produce individual flashes, which may be counted. This gives us another method of determining the period of any element that happens to give off radiations of this type. Furthermore, when a sample of radioactive material is placed in a flask containing moist air, and the air within is suddenly cooled by expansion, the paths of the particles become visible as lines of fog, which may be photographed. The range of the alpha-particles, in air at ordinary pressures, is found to be from 2.37 cm. (uranium I) to 8.16 cm. (thorium C′). From the known number of molecules in a cubic centimeter of air, it has been calculated that these alpha-particles, in traversing the distances given, must collide with hundreds of molecules of oxygen and nitrogen. But since the photographed streaks of fog which show the actual paths of the alpha-particles are practically straight, it is plain that the latter plough their way right through the molecules of oxygen and nitrogen. Thus we have evidence that molecules and atoms are not solid bodies, but complex structures, constructed of smaller particles, between which there appears to exist only empty space. Within the last few years several experimenters have also found evidence that several of the ordinary stable elements, such as nitrogen and aluminum, when bombarded by the alpha-particles of radium are decomposed, producing hydrogen. If this work is confirmed, it will be the first authentic instance of an actual *artificial* transformation of atoms of one element into those of another. For the transformations of radioactivity, though they result in the destruction of atoms of one type and the creation of those of another, are spontaneous, and at present entirely beyond our control.

The Duration of Life on the Earth.—A number of interesting speculations center around the fact that radon and other radioactive substances are present in the soil and in the water of wells and springs in all parts of the earth. Calculation shows that the amount of heat given off during the radioactive decomposition of so much material of this kind as the earth is believed to contain, should be sufficient to make good a large part of the energy that the earth radiates into space. Thus our planet, instead of cooling rapidly through the range of temperature fit for the existence of life, has had this period much prolonged. Some calculations indicate that it may have been habitable for as much as a billion years. Geologists, indeed, from their observations of rocks and fossils, have usually measured the past duration of life upon the earth in hundreds of millions of years.

602. The Metals of the Palladium-Platinum Group.—

VIII			IB
Fe	Co	Ni	63.57
55.84	58.97	58.68	Cu
Ru	**Rh**	**Pd**	Ag
101.7	**102.9**	**106.7**	107.88
Os	**Ir**	**Pt**	Au
190.9	**193.1**	**195.2**	197.2

The palladium-platinum group contains six rare metals: ruthenium, rhodium, and palladium; with osmium, iridium, and platinum. These occur together in nature, in nuggets and grains which may be separated from alluvial sands by washing. The chief deposits are in the Ural mountains, in Russia; though notable amounts come from Colombia; and the United States produces several thousand ounces of platinum each year in the refining of gold bullion. The nickel mattes of Canada (§ 523) furnish a little platinum.

The members of the palladium-platinum group have important relationships to the metals of the iron group, immediately above them in the periodic table, as well as to silver and gold, which occupy adjacent positions at their right.

1. *Vertical Relationships.*—Iron, ruthenium, and osmium are of a darker color than the rest, and melt at higher temperatures. They form oxides (MO and M_2O_3), and, with the exception of iron, other oxides of the general formulas MO_2 and MO_4. (Osmium also forms OsO_3.)

Cobalt, rhodium, and iridium form complex nitrites, such as potassium cobaltinitrite, $K_3Co(NO_2)_6$; and complex cyanides, such as potassium cobalticyanide, $K_3Co(CN)_6$. They form the oxides MO, M_2O_3, and MO_2. Rhodium and iridium differ from the other members of the group in being insoluble in aqua regia.

Nickel, palladium, and platinum form the oxides MO, M_3O_4 (except Pd), and MO_2. Unlike rhodium and iridium, they form stable halides of the general formula MX_2. Palladium and platinum also form complex chlorides, such as K_2MCl_4, and K_2MCl_6, in which they show the valences of two and four, respectively.

2. *Horizontal Relationships.*—The elements of the palladium-platinum group have much higher melting points than those of the iron group.

Ruthenium and palladium are alike in being readily dissolved by fusion with $KHSO_4$. Molten palladium resembles silver in dissolving a considerable volume of oxygen gas.

Osmium, iridium, and platinum resemble gold in their resistance to acids, and in the fact that their salts are readily reduced to metal by mere heating.

603. Platinum.—Platinum is the most abundant and most important of the six metals of the palladium-platinum group. Crude platinum is purified by being dissolved in aqua regia, leaving behind an alloy of osmium and iridium. The solution is evaporated, with addition of sufficient hydrochloric acid to expel the oxides of nitrogen. Addition of ammonium chloride then throws down a yellow, crystalline precipitate of **ammonium chloroplatinate, $(NH_4)_2PtCl_6$**. When this is ignited, metallic platinum remains behind in a spongy form, and may be melted down in an electric furnace, or with an oxy-hydrogen blowpipe.

Platinum, thus prepared, still contains about 2 per cent of iridium, traces of the other metals of the group, and iron. The small amount of iridium has the advantage of making the platinum somewhat harder and more resistant to acids. Metallic platinum is used (1) in dentistry; (2) in the electrical industries, for contact points on spark coils; (3) in jewelry; (4) as a catalytic agent in a number of chemical processes, such as the preparation of nitric acid from ammonia (§ 298) and the manufacture of sulfuric acid (§ 239); and (5) for laboratory apparatus.

The most effective form of platinum for use as a catalyzer is platinum black, prepared by reducing a solution of a platinic salt with formaldehyde, or by precipitating such a solution with metallic aluminum. Platinum black will cause a mixture of hydrogen and oxygen to explode, in consequence of the fact that a part of the gases absorbed in the metal unite rapidly, with liberation of heat. Many important organic reactions, in which hydrogen is used as a reducing agent, take place most readily in the presence of this catalyzer.

Platinum forms three chlorides, $PtCl_2$, $PtCl_3$, and $PtCl_4$. These all dissolve in hydrochloric acid to form **complex acids** tetrachlorplatinous acid, H_2PtCl_4, pentachlorplatinous acid, H_2PtCl_5; and hexachlorplatinic acid, H_2PtCl_6. These all form well-defined crystalline salts, with platinum in the anion. Even such a salt as platinic chloride, $PtCl_4$, when dissolved in water, is largely converted into the acid H_2PtCl_4O, with platinum in the anion. These facts make it evident that **platinum, like gold** (§ 549), **is largely nonmetallic in its chemical behavior.** Platinum forms four different oxides: PtO, Pt_2O_3, Pt_3O_4, and PtO_4; but only PtO and PtO_2 form salts.

604. The Care of Platinum Apparatus.—The high melting-point of platinum, combined with its resistance to acids, makes it very much in demand for crucibles and dishes, for laboratory work. Its chief rivals for this purpose are palau (a palladium-gold alloy), illium (§ 525), and fused silica (§ 400). Platinum has been supplanted by these for many laboratory uses; just as it has been largely replaced in spark terminals, and for winding small electric furnaces, by molybdenum and tungsten; and for leading-in wires of incandescent lights by copper-covered nickel-steel.

Platinum suffers a slight loss in weight when heated for a long time in a blast lamp, on account of volatile impurities. It is extremely resistant to individual acids of all kinds, and to aqueous solutions of salts and alkalies; but it must not be used in presence of:

1. **Aqua regia,** or any other substance (such as $FeCl_3$) **which** yields chlorine on being heated.

2. **Fused caustic hydroxides or peroxides.** (Fused alkali nitrates and acid sulfates attack it slightly.)

3. **Phosphorus, phosphides, or phosphates in the presence of reducing agents,** such as the carbon of filter paper. Many a platinum crucible has been ruined by being used for the ignition of filter-paper containing precipitated phosphates.

4. **Lead, or any other metal that alloys readily with platinum.**—Mercury is safe.

5. **A smoky flame.** This appears to form a carbide of platinum, which is decomposed on further heating, leaving the metal crystalline and brittle.

Platinum ware should be kept clean and bright. One should use moist sea sand for polishing off the crystalline film that sometimes forms on the bottom of a dish or crucible that has been heated for a long time to a high temperature. Stains of iron oxide may be removed by heating strongly with a few crystals of potassium bisulfate, $KHSO_4$.

CONCLUSION

Science is something more than accumulated information. Thus, at the conclusion of a course in General Chemistry, one should have gained something more than a collection of interesting or useful facts. More important than existing knowledge concerning the transformations of matter and energy are the *methods of thought* by which this information has been gained. One may have committed many chemical details to memory without having learned anything of chemistry, if one has failed to catch something of the spirit of the science, or to appreciate the attitude of mind in which a chemist approaches his problems.

It is, indeed, as a product of human thought that chemistry is most impressive. The great peaks that dominate the chemical landscape—the laws that govern the infinite interactions of material things—were discovered for us by the creative efforts of individual men—the master-minds of the past. Thus the universe, from the scintillating sparks of the ultramicroscopic field to the mightiest of flaming suns, has been made to appear as the abode of order.

No less impressive than the laws themselves, as intellectual achievements, are the general theories by which the laws find individual interpretation. Atoms and molecules, protons and electrons—what a world has been revealed beyond the limits of the mechanically aided human senses! Mere smallness hinders the scientist but little, when he sets out to count, weigh, measure, and analyze. Nor are all these triumphs of the past. Chemistry is a *growing* science; and those who labor for its advancement press forward in ever-increasing numbers, with confidence renewed by every new success. On the frontiers of all the principal fields of chemistry are important unsolved problems, and new ones are disclosed with each step in advance.

In studying the ultimate constitution of matter we have learned that an atom is a very intricate structure; but we have not gone far in explaining just what its architecture is, nor why different kinds of atoms, because differently constructed, should have different properties. We have caught certain atoms in the act of exploding, and—wonderfully enough—have identified the fragments of matter thus produced; yet we do not know why only a few elements are so unstable, nor have we learned to hasten or retard the process of disintegration or gain control of the stores of energy thus revealed.

The insight we have gained into the inner structure of molecules has enabled us to synthesize thousands of useful substances; yet in these syntheses we must frequently make use of catalyzers, and we still have no general theory to tell us, in advance of actual trial, what substances should serve this purpose best. Most of our useful reactions are measurably reversible; yet there are but few cases in which we have collected enough information to enable us to calculate how nearly complete they will be under varying experimental conditions.

We have made synthetic dyes quite surpassing any produced by Nature; yet we are fed and clothed by chemical reactions whose details we have hardly begun to understand—those that synthesize carbohydrates in the leaves of green plants, under the influence of the sun's rays. We have produced wonderful synthetic medicines; yet some of our most potent remedies must be obtained, ready-made, from the glands of animals. No one yet knows the chemical nature of the vitamines, nor has anyone yet synthesized an enzyme; and the chemical changes incidental to old age steal upon us just as surely as they did when chemistry and medicine were non-existent. For wood, tannin, and turpentine we still must chop down trees; and still, as in the days of the Cave Men, we slay animals and strip them of their skins. Truly, if the present achievements of chemistry are compared with its possibilities, it is yet in a primitive state.

For those with the rather specialized gifts that productive work in chemistry demands, the field is accordingly limitless. For others, our brief excursion into the realm of strange words and mystic symbols should have yielded souvenirs worth treasuring. The material surroundings of our lives are to-day largely determined by mechanical inventions, made possible by discoveries in chemistry and physics; and the social and economic problems of the day, whose solution is perhaps more pressing than that of any purely scientific problem, will be solved only when large numbers of men and women have learned to consider them without prejudice, applying something of the inductive and experimental methods that have proved so successful in the domain of chemistry. Whatever our occupations, we may well feel a sense of satisfaction in knowing something of a science that has played so important a part in determining the character of the age in which we live. Yet this feeling should be tempered by humility:

"This world, after all our science and sciences, is still a mystery; wonderful, inscrutable, magical, and more, to whosoever will *think* of it."

FIRST GENERAL REVIEW

(CHAPTERS I TO XIV)

1. How could you prove that cupric oxide is a compound, and not an element or mixture?

2. What class of metallic oxides yield oxygen when heated? Name several.

3. Describe tests by which you could distinguish between potassium chloride, potassium chlorate, and potassium perchlorate.

4. Formulate the reactions, if any, that take place when magnesium, aluminum, copper, potassium, silver, and iron are acted upon by dilute hydrobromic, sulfuric, and phosphoric acids. Name the salts produced.

5. Four bottles contain respectively O_2, air, CO_2, SO_2. How would you identify each?

6. What weight of air is needed for complete combustion of a pound of coal containing 85 per cent carbon, 12 per cent hydrogen, 3 per cent ash?

7. How would you determine the percentage of acetic acid in vinegar? Of hydrogen in filter paper? Of oxygen in copper oxide?

8. Write and balance equations for the following:

(*a*) Metallic antimony burns in a limited amount of air.

(*b*) Manganese dissolves in hydriodic acid.

(*c*) Magnetic iron oxide is reduced by hydrogen.

(*d*) Metallic calcium acts on water, liberating hydrogen.

(*e*) Cuprous oxide is oxidized by air.

(*f*) Ozone acts on a solution of magnesium iodide.

(*g*) Hydrobromic acid is oxidized by lead dioxide.

(*h*) Sodium peroxide reacts with dilute hydrochloric acid, by double decomposition.

9. Two oxides of an element, X, contain respectively 50 per cent and 60 per cent oxygen. Calculate the weight of X united with 16 parts of oxygen in each case. Show that the result illustrates one of the laws of weight relations.

10. Calculate the weight in grams of a liter of each of the following: Chlorine, hydrogen chloride, air, helium.

11. If 1 g. of an element, X, forms 1.3285 g. of a chloride, XCl, calculate the atomic weight of X.

12. Calculate the number of cubic feet of air required to convert 1 ton of coke (10 per cent ash) into carbon monoxide.

13. What is meant by aqueous tension? On what does it depend? How may it be measured?

14. Moisture collects on the outside of a pitcher of ice-water in summer but not in winter. Explain.

15. Write an equation for the preparation of chlorine from bleaching powder. What volume of chlorine at standard conditions should be obtained from a pound of commercial bleaching powder, assumed to contain 25 per cent moisture and $Ca(OH)_2$, as impurities?

16. If a liter of chlorine gas is dissolved in water and the solution exposed to sunlight, what volume of gas will be evolved? How many grams of NaOH will be required to neutralize the acid thus formed?

17. Write formulas of the following substances, indicating the valence (+ or −) of each element: Ferrous perchlorate, ammonium iodate, ammonium dichromate, magnesium hypobromite, manganous hydroxide. What is the algebraic sum of the valence units in each molecule?

18. What kinds of information need to be obtained before the formula of a compound may be determined? Illustrate for H_2O.

19. Write and balance equations for the formation of the following insoluble salts by double decomposition between soluble salts or a salt and a base: Zinc phosphate, mercuric iodide, calcium oxalate, stannic sulfide, barium chromate, aluminum hydroxide.

20. A liter of air is ozonized, the reaction being 10 per cent complete. What weight of ozone does it then contain? What volume does it then occupy?

21. What physical or chemical properties of the substances concerned determine the following uses: Gold for filling teeth, mercury in thermometers, chlorine as a disinfectant, tin for wrapping confectionery, gold tipped with iridium for fountain pens, linoleum for flooring, ice as a refrigerant, superheated steam as a source of heat?

22. Describe conditions under which the following reactions are complete and conditions under which they remain incomplete: Action of chlorine on water, water decomposed by metallic magnesium, action of sulfuric acid on common salt, direct union of hydrogen and iodine to form hydriodic acid.

23. List a few metals in the order in which they occur in the electrochemical replacement series. Explain the use of this series.

24. Give equations for the preparation of magnesium sulfate by several methods, different in principle.

25. Distinguish between acid salts, basic salts, and normal salts, with examples.

26. Give a synopsis of the distinction between the different states of matter, in terms of the atomic and molecular theories.

27. A liter of sulfuric acid, 95 per cent pure, contains enough acid to neutralize 1750 g. of caustic soda, 80 per cent pure. What is the specific gravity of the acid?

28. What weight of zinc is chemically equivalent to 0.63 g. of nitric acid?

29. Formulate your best guess concerning what happens in each of the following cases, indicating the reason for your answer: Sodium iodate heated; aluminum burned in air; chlorine passed into a cold solution of barium hydroxide; sulfur oxidized by ozone; iron dissolved in hydrofluoric acid; barium carbonate dissolved in acetic acid.

30. Describe a quantitative synthesis of water, and indicate why the result is of importance.

SECOND GENERAL REVIEW

(CHAPTERS XV TO XXX)

1. Name an element that has both metallic and non-metallic properties, and give some of the evidence.

2. Two sulfides contain respectively 33.52 per cent and 20.14 per cent sulfur. If the first is represented by the formula MS, show that the other must be M_2S.

3. Show that the different oxides of nitrogen illustrate the Law of Related Composition.

4. Which of the following gases are lighter than air, and which heavier, and in about what proportion: Carbon dioxide, nitrous oxide, phosphine, phosgene, methane?

5. State the law relating to the relative volumes of combining gases.

6. Indicate briefly how the molecular weight of each of the following substances has been determined; or, if it has not been determined, tell why: ammonia, glucose, sodium sulfite, graphite, manganese dioxide, crystalline KBr.

7. Explain how it is determined that chlorine should be represented by the formula Cl_2.

8. A gas measures 35.4 cc., over water, at 25° C., the barometer reading 746 mm. What will be its volume, dry, at standard conditions?

9. A glass bulb holding 135 cc. is filled with vapor at 98° C., and then sealed off, the barometer reading 740 mm. The weight of the vapor is found to be 351 mg. What is the molecular weight of the substance?

10. Is the value obtained in the preceding problem an exact or approximate molecular weight, and why?

11. Explain the relation between combining weights and atomic weights. The combining weight of a metal is known to be 31.78. What further information is needed to determine its exact atomic weight, and how is this information obtained?

12. Compare the rates of diffusion of hydrogen and helium through the fabric of a balloon.

13. Explain why $O=16$ is taken as the basis of our modern system of atomic weights.

14. What are some of the most important industrial applications of the following: liquid air, elementary sulfur, alcohol, nitric acid, sulfuric acid, ammonia and ammonium salts?

15. Give formulas for two amphoteric oxides. Give equations to illustrate the acid and basic behavior of one of them.

16. One hundred cc. of hydrochloric acid, sp. gr. 1.175, containing 34.5 per cent HCl, will prepare what volume of N/10 solution?

17. Give equations to explain how ozone turns starch-potassium iodide paper blue. Name several other substances having the same property.

18. A certain gas, heated from 273° A. to 546° A., expands to much more than twice its original volume. What explanation can you give?

19. A solution containing 42 g. of a non-electrolyte in 1 liter freezes at -0.31° C. What is its approximate molecular weight?

20. Explain how the degree of ionization of a salt can be determined from freezing-point measurements; from conductivity measurements.

21. Which freezes at the lower temperature and why; a solution containing 58.5 g. of common salt or one containing 92 g. of glycerol in the same weight of water?

22. What kinds of salts hydrolyze in water: (*a*) completely; (*b*) incompletely; (*c*) practically not at all? Illustrate with several examples of each.

23. How may the following be prepared from substances found in nature: sodium nitrite, ethyl acetate, carborundum, glycerine, ammonium sulfate, orthophosphoric acid, boric acid?

24. Write equation for the preparation of HF from apatite.

25. Tell what differences are observed in decomposing the different sodium halides with concentrated sulfuric acid. Explain.

26. What are the circumstances that determine the speed of chemical reactions? Why are certain reactions incomplete? How may they be made more complete? Illustrate by the synthesis of ammonia.

27. What reaction, if any, would you expect to take place between the following substances, and why: hydriodic and nitric acids; bromine and zinc chloride; ozone and hydrobromic acid; metaphosphoric acid and starch?

28. Give formulas of three potassium salts containing both chlorine and oxygen. (*a*) State how each is prepared; (*b*) how identified; (*c*) how made to produce chlorine.

29. List six acids in the order of decreasing activity. How is the difference in activity explained on the basis of the ionic theory?

30. How would you proceed to convert powdered sulfur as completely as possible into H_2S?

31. Give name and formula of one oxidizing and one reducing agent containing each of the following elements: H, I, S, N, As, C. Write equations to illustrate the oxidizing or reducing property of each substance you have mentioned.

32. A solution is known to contain one of the following salts: KNO_3, $AlCl_3$, Na_2CO_3, $CaCl_2$, NaBr. It is found to be neutral to litmus, and no color change takes place on adding conc. H_2SO_4, either alone or with a few drops of $FeSO_4$ solution. Which salt is indicated? Explain in detail.

33. How would you prepare hydrogen from H_2S? Sulfur from H_2S? Write equations.

34. Explain the meaning of the italicized words in the following quotation: "The *normal* sodium salt is *anhydrous*, but quite *hygroscopic*, and even *deliquescent*. If it is heated with an *equivalent amount* of a *non-volatile inorganic* acid, a gas is expelled which is the *anhydride* of a *dibasic acid*. In *aqueous* solution this acid shows but slight *electrolytic dissociation*."

35. Distinguish between the momentary and total acidity of a solution. How is each determined?

36. What properties distinguish a true from a colloidal solution?

37. How may each of the following substances be prepared from ammonia: nitrogen; hydrogen; nitric acid; ammonium arsenite; ammonium bicarbonate; nitric oxide? Write equations.

38. Show what happens when cane sugar is converted successively into invert sugar, alcohol, acetic acid.

39. The vapor density of a certain metallic chloride is about thirteen times the density of air. What conclusions can be drawn concerning its approximate molecular weight? The compound contains about 38.11 per cent chlorine. What is the maximum possible atomic weight for the other element, X? Assuming this to be the true atomic weight, what is the formula of the compound?

40. If a new form of chlorine were discovered such that one volume united with $1\frac{1}{2}$ volumes of hydrogen to form hydrogen chloride, what would be its molecular formula? What would be the approximate weight of 1 liter of this gas, at standard conditions? What volume of hydrogen chloride could be produced from one volume of the gas?

41. Pure benzene freezes at 5.48°. A solution of 3.2 g. of naphthalene in benzene freezes at 3.48° C. When 2.45 g. of another substance is dissolved in the same weight of benzene as was used for dissolving the naphthalene, the solution freezes at 3.75°. What is the molecular weight of the second substance? Naphthalene is $C_{10}H_8$.

42. What volume of carbon monoxide, at 25° C. and 750 mm. pressure, is obtainable from a gram of carbon? What volume of air is consumed in the preparation of this carbon monoxide?

43. Determine the relative volumes of the individual reactants and resultants when alcohol vapor is burned with a 50 per cent excess of oxygen.

44. Recalling the chemical inertness of nitrogen, what would you presume the products to be when cyanogen is burned in an excess of oxygen? What are the relative volumes of the four gases concerned?

45. A liter of a certain gas weighs about 2.32 g. It contains 46.08 per cent of carbon, and the rest nitrogen. What is its formula?

46. Write and balance equations for the oxidation of HCl with MnO_2, $KMnO_4$, and $K_2Cr_2O_7$, respectively. If a 50 per cent excess of HCl is used, what percentage of the total chlorine is liberated in each case in the elementary form?

47. Write and balance equations for the following:
(*a*) Action of metallic magnesium on water.
(*b*) Potassium nitrate is heated.
(*c*) Action of sunlight on hypochlorous acid.
(*d*) Action of sulfuric acid on salt.
(*e*) Preparation of acetylene from calcium carbide.
(*f*) Phosphorus burned in air.
(*g*) Hydrolysis of a phosphorus halide.

48. Classify the preceding reactions as direct combination, decomposition, dissociation, double decomposition, substitution, displacement, oxidation and reduction.

49. Coke is burned to carbon monoxide and the heat liberated is absorbed in bringing about the reaction of an additional quantity of coke with steam to form water gas. Write equations. Calculate the percentage by volume of each gas in the final mixture of gases from the two reactions, if 0.5 lb. of coke is consumed in the first reaction for every 1.0 lb. in the second.

50. What are the three principal sources of commercial gasoline? Explain how the heating value of a fuel is determined. Is the heating value a measure of the "miles per gallon" obtainable with a given car? Discuss the various factors that enter into this question.

51. Which of the following reactions are complete and why; which incomplete and why?

Direct union of hydrogen and oxygen; precipitation of $AgNO_3$ by HCl; precipitation of $ZnCl_2$ by H_2S; decomposition of NH_3 by heat; action of chlorine on water; neutralization of HCl by NaOH.

52. Why can magnetic iron oxide be completely reduced by a stream of hydrogen, in spite of the fact that the reverse reaction, oxidation of iron, is complete in a current of steam?

53. By what means other than an increase in temperature can the dissociation of iodine vapor, $I_2 \rightleftarrows 2I$, be made more complete?

54. Explain why the combination of nitrogen and hydrogen to form ammonia is made more complete by an increase of pressure, while that of iodine and hydrogen to form hydrogen iodide is not.

55. The vapor of mercurous chloride is completely dissociated into metallic mercury and chlorine at high temperatures. What ratio does the density of the resultant mixture bear to that calculated from the formula Hg_2Cl_2?

56. Calculate the density of the vapor of PCl_5 at 200° C., under a pressure of 740 mm., assuming 50 per cent dissociation into PCl_3 and Cl_2.

57. What weight and volume of hydrogen bromide can be prepared with 3.1 g. of red phosphorus, by way of PBr_5?

58. Acetylene can be synthesized by passing hydrogen through an electric arc with carbon electrodes. The reaction absorbs heat. Will it become more or less complete with an increase of temperature? State the principle involved.

59. In tenth normal solution, potassium chloride is 85 per cent ionized. What is the freezing-point of the solution?

60. What is the degree of ionization of sodium acetate, if 1.025 g. of the anhydrous salt, dissolved in 125 g. of water, produce a solution freezing at $-0.350°$?

61. The freezing-point of a 3.7 per cent solution of hydrogen peroxide in water is $-2.03°$. Does the substance appear to be electrolytically dissociated in solution, and if so to what extent?

62. What is the reaction toward litmus of a solution of calcium sulfide? Explain in terms of the ionic theory.

63. Tell what things need to be considered in selecting an indicator for titrating an acid by a base. What are the proper uses of phenolphthalein and thymol blue?

64. By reference to the table of solubilities find a case in which two soluble salts enter into double decomposition to form a pair of salts *both of which are insoluble*.

65. Fifty cc. of a solution of sodium hydroxide requires 27.8 cc. of N/10 acid in titration. What is its normality, and how many milligrams of NaOH are contained in each cubic centimeter?

66. Formulate, both molecularly and ionically:

(*a*) Action of metallic calcium on water.

(*b*) Action of iodine on hydrogen sulfide.

(*c*) Formation of sodium thiosulfate from sodium sulfite.

(*d*) Oxidation of stannous chloride by chlorine.

67. Explain the use of the two towers in the chamber process for making sulfuric acid, as a case of reversible reaction.

68. What is a perfect gas? State its most important properties.

69. A gas is confined within a definite volume at 27° C. To what temperature must it be raised in order to double the pressure that it exerts?

70. What is wrong with the following statements? Give the correct statement in each case:

(*a*) The boiling point of a liquid is the temperature at which it passes into vapor.

(*b*) A crystal is a solid body, with a definite type of symmetry, bounded by plane surfaces meeting at definite angles.

(*c*) A saturated solution is one that contains as much of the given dissolved substance as it can be made to contain at the given temperature.

(*d*) Equilibrium is the situation existing when a reaction has been brought to a stop.

(*e*) The law of related composition is illustrated by the fact that the percentages of oxygen in the different lead oxides are simply related to each other.

71. The air in a 10-liter bottle is saturated with water vapor at 25° C., and 740 mm. pressure. What would be the weight of this moisture if it were all condensed (*Appendix A*)?

72. What is the simplest possible formula of a substance containing 78.89 per cent carbon, 10.66 per cent hydrogen, and the rest oxygen? What other information needs to be given in order to obtain the true formula? For what kinds of substances may this other information be obtained?

73. Calculate the weights of a liter of pure nitrogen and a liter of nitrogen containing 1 per cent by volume of argon.

74. A fire extinguisher contains 5 kg. of sodium bicarbonate. What weight of pure sulfuric acid is necessary to decompose it, with the formation of sodium bisulfate? What volume of carbon dioxide is liberated, at standard conditions?

75. Ten liters of air, bubbled through a solution of barium hydroxide, produced a quantity of barium carbonate equivalent to 10.8 cc. of N/40 acid. Calculate the percentage of carbon dioxide in the air, by volume.

76. If glycerol and methyl alcohol sold at the same price, which would be the better for preparing an anti-freeze solution for the radiator of an automobile? State the principle involved.

77. From the method of preparing each of the following substances, what impurities would you expect it to contain:

$NaOH$, H_2SO_4, HNO_3, $KClO_3$?

78. What are the most noteworthy differences in the properties of Na and Na^+; of Cl_2 and Cl^-; of Cl^- and ClO_3^-?

79. Normal solutions are prepared of HAc, HCl, NH_4OH, and Na_2SO_4. Which of these will conduct the electric current best? Explain.

80. Explain how the valence and metallic or non-metallic nature of an element may be determined from its position in the periodic table.

81. Distinguish between liquid hydrogen chloride and hydrochloric acid.

82. List a few simple compounds of germanium, from its position in the periodic table.

83. How may the sign of the electrical charge on a colloidal particle be determined?

84. What are the following minerals, and for what are they used: Gypsum, pyrite, galena, quartz, Chile saltpeter, colemanite, phosphate rock, feldspar, kaolin, diamond, arsenopyrite?

85. Heating silica with carbon may produce either silicon or carborundum. Explain.

86. What is adsorption? Give applications in at least two industries.

87. Give reasons for believing in the actual physical existence of atoms and molecules.

THIRD GENERAL REVIEW

(CHAPTERS XXXI TO XLIV)

1. Tell whether the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine is rendered more or less complete (*a*) by an increase of temperature; (*b*) by an increase of pressure. State the principle involved.

$$PCl_5 \rightleftarrows PCl_3+Cl_2+33{,}000 \text{ cals.}$$

2. By what single test could you distinguish between the following:

(*a*) MnO_2 and charcoal.
(*b*) $CaCO_3$ and CaC_2O_4.
(*c*) $CuCl_2$ and $NiCl_2$.
(*d*) $MnCl_2$ and $CoCl_2$.
(*e*) $K_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$.
(*f*) $CaCl_2$ and $MgCl_2$.
(*f*) HIO_3 and $H_2C_2O_4$.

Tell what happens in each test, and write an equation for any reaction that may take place.

3. How could you free air from the following, on a laboratory scale:

(*a*) Dust and bacteria.
(*b*) Moisture.
(*c*) Ammonia.
(*d*) Carbon dioxide.
(*e*) Oxygen.

4. Give the percentage by volume of each gas in a mixture formed by burning carbon in twice the quantity of air needed for its complete combustion.

5. How would you prepare pure carbon dioxide from such a mixture—(*a*) on a laboratory scale; (*b*) commercially?

6. Write equations for the reactions, if any, that you believe will take place.

(*a*) When an excess of sulfur dioxide is passed into a solution of ammonia.
(*b*) When arsenic trisulfide is heated with potassium chlorate (*danger*).
(*c*) When calcium carbide is heated with copper oxide.
(*d*) When aniline vapor is burned in an excess of air.
(*e*) When ammonium iodide is ignited.

7. Given metallic lead and metallic chromium, how would you prepare lead chromate? Write and balance all equations.

8. Given metallic barium and elementary arsenic, how would you prepare barium arsenate?. Write and balance all equations.

9. All of the following formulations are incorrect. In each case tell what principle applies, and give the correct formulation:

(*a*) $KCl+HNO_3 \text{ (conc.)} \rightarrow KNO_3+HCl.$
(*b*) $2KBrO_3+Cl_2 \rightarrow 2KClO_3+Br_2.$
(*c*) $H_3PO_4+Cu \rightarrow Cu_3(PO_4)_2+H_2$
(*d*) $NaCl+H_2O \rightarrow HCl+NaOH.$
(*e*) $AgCl+HC_2H_3O_2 \rightarrow AgC_2H_3O_2+HCl.$

(*f*) $H_2SO_4+NaI \rightarrow NaHSO_4+HI$.
(*g*) $Cl_2+2KOH \rightarrow 2KCl+H_2O_2$.
(*h*) $2FeCl_3+3H_2S \rightarrow Fe_2S_3+6HCl$.
(*i*) NH_4OH (excess)$+CuSO_4 \rightarrow Cu(OH)_2+(NH_4)_2SO_4$.
(*j*) $2HCl+BaSO_4 \rightarrow BaCl_2+H_2SO_4$.
(*k*) $H_2+S \rightarrow H_2S$.
(*l*) $Cu(NO_3)_2+H_2S \rightarrow CuS+2HNO_3$.
(*m*) $2AlCl_3+3H_2S \rightarrow Al_2S_3+6HCl$.
(*n*) $3H_2CO_3+2As(OH)_3 \rightarrow As_2(CO_3)_3+6HOH$.
(*o*) $Cu+CdSO_4 \rightarrow CuSO_4+Cd$.
(*p*) NH_4NO_3 (heated) $\rightarrow NH_3+HNO_3$.
(*q*) $HC_2H_3O_2+KCl \rightarrow KC_2H_3O_2+HCl$.
(*r*) $6HF+O_3 \rightarrow 3H_2O+F_2$.
(*s*) $HCl+O_3 \rightarrow HClO+O_2$.
(*t*) $KI+HNO_2+H_2O \rightarrow KIO_3+NH_3$.
(*u*) $2FeSO_4+2H_2SO_4 \rightarrow Fe_2(SO_4)_3+2H_2O+SO_2$.
(*v*) $FeCl_3$ (acid sol.)$+H_2S \rightarrow Fe_2S_3+HCl$.
(*w*) $K_2CrO_4+HCl \rightarrow KCl+CrCl_3+H_2O$.
(*x*) $ZnCl_2+H_2O+CO_2 \rightarrow ZnCO_3+2HCl$.

10. Pyrite is roasted in twice the quantity of air needed for complete oxidation. Calculate the percentage by volume of each gas in the mixture of gases thus produced.

11. What are the raw materials used in the production of pig iron in the blast furnace? Give a brief description of the process, with balanced equations.

12. Describe the production of metallic aluminum from an impure aluminum mineral, with equations.

13. Give an outline of the production of metallic copper from a low-grade copper ore, with equations.

14. Describe the preparation of white lead, with equations. For what is this substance used?

15. What are the chemical names and uses of the following: galena, emery, litharge, lithopone, hematite, carborundum, quartz, kaolin, gypsum, graphite?

16. State and illustrate the distribution law.

17. What is meant by isomeric substances? Illustrate.

18. How is cane sugar inverted? Write equation.

19. Name two reducing sugars and one non-reducing sugar. By what test can reducing sugars be distinguished from non-reducing sugars?

20. How would you separate mixtures of the following gases, obtaining each on a commercial scale, in a reasonably pure condition (Appendix C):

(*a*) CO and CO_2;
(*b*) SO_2 and O_2;
(*c*) Cl_2 and air;
(*d*) H_2 and NH_3;
(*e*) N_2 and NO_2.

21. Name a chemical absorbent which might be used on a laboratory scale to separate the gases in each of the preceding cases, and indicate how the gas absorbed might afterwards be recovered.

22. Determine the approximate density with respect to air of a sample of coal gas containing 50 per cent hydrogen, 35 per cent methane, 10 per cent carbon dioxide, and 5 per cent nitrogen, by volume.

23. State and illustrate the laws and principles connected with the names of the following:

Avogadro, Boyle, Charles, Dalton, Faraday, Gay-Lussac, Henry, Le Chatelier, Van't Hoff, Priestley.

24. Show that Henry's Law is consistent with the Principle of Le Chatelier.

25. How would you determine experimentally whether the element beryllium has the properties of a metal or a non-metal?

26. Write ionic equations for: (*a*) dissolving iron in hydrochloric acid; (*b*) action of zinc on a solution of silver nitrate; (*c*) electrolysis of a solution of common salt; (*d*) the precipitation of a calcium salt by ammonium oxalate; (*e*) neutralization of calcium hydroxide by acetic acid.

27. Indicate the electronic changes in the reactions of the preceding question.

28. Calculate the freezing-point of a solution of 10 g. of acetone in 100 g. of water. State the principle involved.

29. Summarize the principal experimental evidence in support of the ionic theory.

30. What is the effect of a slight amount of lead nitrate on the solubility of lead sulfate in water? Explain.

31. List six metals in the order of decreasing activity. How is the difference in activity explained on the basis of the electronic theory?

32. Formulate and explain one good example of each of the following in terms of the ionic theory: (*a*) neutralization; (*b*) precipitation; (*c*) repression of the ionization of an active acid by the addition of a salt of an inactive acid; (*d*) displacement of a metal from a solution of one of its salts by a more active metal; (*e*) deposition of a heavy metal by electrolysis, from a solution of one of its salts.

33. How many cubic centimeters of normal acid are needed to neutralize the alkali produced by the passage of a current of 1 ampere for one hour through a solution of common salt?

34. How long will it take a current of 5 amperes to deposit a layer of silver 0.1 mm. thick over an area of 100 sq. cm.? The specific gravity of silver is 10.5.

35. A cubic centimeter of hydrogen gas, measured dry at 25° C. and 740 mm. pressure, corresponds to what fraction of a mole of hydrogen? What fraction of a milligram-equivalent? How many coulombs of electricity will be needed to liberate this much hydrogen, by electrolysis of water?

36. Give electronic equations to represent the chemical changes taking place at each of the plates of a lead storage cell, during charge and discharge, respectively.

37. In what way is the development of a stain of metallic copper, on a sheet of zinc placed in a copper sulfate solution, the same in principle as the reaction that takes place when zinc dissolves in an acid?

38. Write electronic equations to represent the change at each of the electrodes when the following solutions are electrolyzed between graphite electrodes: potassium iodide, potassium sulfate, silver sulfate, acetic acid, sodium hydroxide.

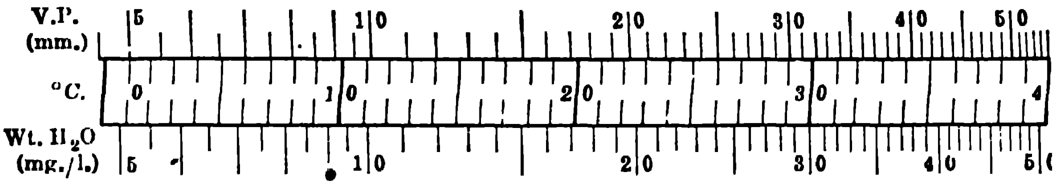
39. What weight of barium peroxide is necessary to prepare 1 liter of hydrogen peroxide solution, of sp. gr. 1.15, containing 30 per cent H_2O_2?

40. Compare the rate at which an electric current of given strength will deposit iron from ferrous and ferric solutions, respectively.

APPENDIX

A. VAPOR PRESSURE OF WATER

THE middle scale gives temperatures on the centigrade scale. The upper scale shows the vapor pressure of water at each temperature, and the lower scale the number of milligrams of water in one liter of saturated air.



B. COMPOSITION AND FUEL VALUE OF FOODS

Data chiefly from Sherman, "Chemistry of Food and Nutrition" (Macmillan)

	Percentage Composition			*Large Calories per Pound*
	Protein	*Fat*	*Carbo-hydrate*	
Apples	0.4	0.5	14.2	285
Bacon (smoked)	10.5	64.8		2840
Beans, dried	22.5	1.8	59.6	1565
Beans, baked, canned	6.9	2.5	19.6	583
Beef, medium fat	15.8	28.5	...	1450
Beef, flank, lean	20.8	11.3		838
Bread, white, homemade	9.1	1.6	53.3	1200
Butter	1.0	85.0	.	3490
Cabbage	1.6	0.3	5.3	143
Cheese, American pale	28.8	35.9	0.3	1990
Chicken (broilers)	21.5	2.5	...	493
Corn, green, canned	2.8	1.2	19.0	455
Corn meal	9.2	1.9	75.4	1620
Eggs, uncooked	13.4	10.5	. .	672
Flour, wheat, average	11.4	1.0	75.1	1610
Ham, fresh, lean	25.0	14.4	.	1042
Hominy	8.3	0.6	79.0	1609
Macaroni	13.4	0.9	74.1	1625
Milk, whole	3.3	4.0	5.0	314
Oatmeal	16.1	7.2	67.5	1811
Peaches, canned	0.7	0.1	10.8	213
Potatoes, white, raw	2.2	0.1	18.4	378
Rice	8.0	0.3	17.9	1590
Shredded wheat	10.5	1.4	77.9	1660
Sugar	...	....	100.0	1815
Turnips	1.3	0.2	8.1	178
Walnuts	18.4	64.4	13.0	3200

C. PROPERTIES OF SOME COMMON GASES

GASES DIFFICULT TO LIQUEFY

(formerly called permanent gases)

	Melting Point	*Boiling Point*	*Critical Temperature*	*Critical Pressure*	*Chief Chemical Characteristics*
Argon, A	−188	−186.1	−117.4	52.9	Completely inert
Helium, He	−272	−268.8	−268	23	Completely inert
Hydrogen, H_2	−259	−252.8	−234.5	20	Reducing agent at higher temps.
Methane, CH_4	−184	−164	− 95.5	50	Combustible
Nitrogen, N_2	−210.5	−195	−146	33	Inert, except at higher temps.
Oxygen, O_2	−218	−182.7	−118	50	Unites directly with metals and non-metals
Carbon monoxide, CO	−207	−190	−141.1	35.9	Poisonous; combustible

GASES EASY TO LIQUEFY

(formerly called condensible gases)

	Melting Point	*Boiling Point*	*Critical Temperature*	*Critical Pressure*	*Chief Chemical Characteristics*
Acetylene, C_2H_2	− 81	− 85	36.5	61.6	Unsaturated (§ 340); combustible
Ammonia, NH_3	− 77	− 38.5	130	115	Unites directly with water and acids; decomposed at a red heat
Carbon dioxide, CO_2	− 57	− 79	31.1	73	Acid anhydride; reduced by hot carbon to CO
Chlorine, Cl_2	−101.5	− 33.6	146	93.5	Unites direct with metals and non-metals; oxidizing agent
Ethylene, C_2H_4	−169	−102.7	+ 10	51.7	Unsaturated; combustible; useful in anesthesia
Hydrogen chloride HCl	−112.5	− 83.1	52.3	86	Extremely soluble in water; solution has properties of an active acid
Hydrogen sulfide. H_2S	− 85.5	− 61.8	100	88.7	Reducing agent; inactive acid; precipitant; decomposed when heated
Nitrogen peroxide	− 9.6	21.6	171.2	147	Oxidizing agent
Nitrous oxide, N_2O	−102.4	− 89.4	38.8	77.5	Supports combustion; useful in anesthesia
Sulfur dioxide, SO_2	− 72.7	− 10	155.4	78.9	Acid anhydride; reducing agent; bleaching agent

D. PREPARATION OF COLLOIDAL SOLUTIONS

It is believed that any substance whatever may be obtained in colloidal form in any liquid in which it does not form a true solution. A summary of the chief methods for preparing colloidal solutions will serve as a review of some of the principles discussed in Chapter XXVIII.

I. Condensation Methods. (Particles increase in size from molecular to *colloidal dimensions.)*

1. Reduction.

Solutions of	*Reacting with*	*Stabilized by*
$AuCl_3$	formaldehyde	gelatin
$PdCl_4$	hydrazine	gum arabic

2. Oxidation.

H_2S by	SO_2	gelatin

3. Double Decomposition.

As_2O_3	H_2S	gelatin
$AgNO_3$	KBr	excess $AgNO_3$ or HBr
$FeCl_3$	$K_4Fe(CN)_6$	gelatin
$NiCl_2$	H_2S	Na_2S
$AgNO_3$	K_2CrO_4	casein
$CuSO_4$	NaOH	glycerol
$FeCl_3$	NH_4OH	cane sugar
$BaCl_2$	Na_2SO_4	sodium citrate

4. Hydrolysis.

dilute $FeCl_3$	boiled	(dialysis)
dilute $Al(C_2H_3O_2)_3$	boiled	(dialysis)

II. Dispersion Methods.

Solutions of	*Reacting with*	*Stabilized by*
1. Mechanical Dispersion.		
metals	water	gelatin or honey
graphite	water or oil	tannin

2. Addition of Peptizing Agent.

Material	*Dispersed in*	*Peptized by*
clay	H_2O	NH_4OH
silicic acid	H_2O	NaOH
Prussian blue	H_2O	$H_2C_2O_4$
$Al(OH)_3$	H_2O	NaOH
graphite	H_2O	tannic acid
carbon	mineral oil	tar oil, creosote
coal.	mineral oil	tar, rosin oil

3. Removal of Agglomerating Agent.

Many precipitates (AgCl, rare earth hydroxides, ZnS, H_2SnO_3) tend to pass into colloidal solution and run through the filter paper as soon as adsorbed electrolytes are washed out. The analytical chemist therefore washes precipitates with suitable solutions of electrolytes, rather than with pure water.

4. **Electrical Disintegration (Bredig's Method).**

   A direct current arc (30 to 50 volts) is struck under water between electrodes of Pt, Au, Ag, Cd, etc. Disintegration is chiefly at cathode.

5. **Electrochemical Disintegration.**

   Observed on electrolysis of molten salts or alkaline solutions, with metallic electrodes.

E. SOME NOTEWORTHY EVENTS IN THE HISTORY OF CHEMISTRY

About 500 B.C.	Democritus and other Greek philosophers taught that matter is composed of indivisible and indestructible atoms.
About A.D. 765	Geber (born in Mesopotamia or Persia; lived in Seville) described nitric acid, sulfuric acid, and aqua regia, and studied their action on metals.
1660–1680.	Boyle, Robert (Ireland), discovered the law of compressibility of gases; directed attention to the increase in weight that is experienced by metals when they are oxidized by heating in the air; noted distinguishing properties of a class of substances which he called "salts"; and distinguished between elements and compounds.
1755.	Black, Joseph (England), studied magnesium oxide and magnesium salts; introduced quantitative methods into chemical investigations; discovered many facts concerning carbon dioxide, carbonic acid, and its salts.
1766.	Cavendish, Henry (England), performed experiments on hydrogen, carbon dioxide, and air.
1771–1777.	Scheele, Carl Wilhelm (Sweden), discovered oxygen, chlorine, nitrous oxide, hydrogen sulfide, and many other important substances.
1774–1777.	Lavoisier, Antoine Laurent (France), performed experiments on the oxidation of tin when heated in the air, and on the formation and decomposition of mercuric oxide (§ 47). As a result of this work he was able to give the first clear explanation of the nature of oxidation and combustion.
1774–1777.	Priestley, Joseph (England), made the first thorough study of the methods of preparation and chemical properties of oxygen gas. In connection with this he devised important methods for the manipulation of gases.
1783–1787.	Lavoisier and others (France) discovered the composition of water; developed the modern system for naming chemical substances.
1792–1794.	Richter, J. B. (Germany), discovered the law of combining weights.
1801.	Nicholson and Carlisle (England) decomposed water by electrolysis.

1801–1815.	Hare, Robert (America), invented the oxyhydrogen blowpipe (§ 59) and the electric furnace.
1807–1810.	Davy, Sir Humphry (England), discovered the alkali and alkaline earth metals (§§ 430, 446); proved the elementary nature of chlorine (§ 175).
1808.	Dalton, John (England), published his atomic theory.
1809.	Gay-Lussac, Louis Joseph (France), published his observations on the proportions by volume in which gases combine (Law of Gay-Lussac, § 89).
1810.	Gay-Lussac developed the method now in use for the analysis of organic compounds by combustion (§ 40).
1811.	Avogadro, Amadeo (Italy), published his principle (§ 22).
1811–1819.	Berzelius, Jöns Jacob (Sweden), performed accurate experiments to confirm the laws of related composition (§ 90) and combining weights. He also introduced the modern system of chemical symbols; drew up the first fairly complete and accurate table of atomic weights.
1819–1832.	Mitscherlich, Eilhardt (Germany), directed attention to the resemblances between the crystal forms of substances of related chemical composition.
1831–1839.	Liebig, Justus von (Germany), performed numerous important researches on the composition and chemical reactions of organic substances; was the first to recognize the existence of organic radicals.
1834.	Faraday, Michael (England), published the results of his electrochemical researches, including his law of electrolysis (§ 428).
1839.	Dumas, Jean Baptiste (France), directed attention to resemblances between the formulas of various organic and inorganic substances. This work (theory of types) later developed into structural formulas (§§ 124, 342).
1841–1881.	Stas, Jean Servais (Belgium), devoted many years to the accurate determination of atomic weights. Many of his values have stood, with trifling corrections, down to the present day.
1856.	Perkin, Sir William (England), discovered the first coal-tar dye (§ 372).
1858.	Cannizaro (Italy) showed how molecular and atomic weights may be derived, by a system of reasoning based on the principle of Avogadro. It then became possible, for the first time, definitely to establish chemical formulas as they are written to-day.
1858–1867.	Deville, Saint-Claire (France), studied dissociation (§ 157) as a reversible reaction.
1860–1861.	Bunsen and Kirchoff (Germany) developed the spectroscope; and with its aid discovered rubidium and cesium.

1865.	Kekulé, August (Germany), worked out the structural formula of benzene, and thus laid the foundations of the chemistry of the aromatic compounds.
1867.	Guldberg and Waage (Sweden) gave the first clear statement of the law of mass action (§ 214).
1871.	Mendeléjeff, Dmitri Ivanovitch (Russia), and Meyer, Lothar (Germany), made independent discovery of the periodic law (§ 173).
1872.	Pasteur, Louis (France), published his work on the production of chemical changes by microorganisms.
1876.	Gibbs, Willard (America), laid the foundations of the application of thermodynamics to chemistry. Some of the most important recent progress in physical chemistry has been based upon his work.
1882–1887.	Raoult, François Marie (France), established the laws that determine the freezing points, boiling points, and vapor pressures of solutions of non-electrolytes (§ 99).
1884.	Le Chatelier (France) stated his principle of equilibrium (§ 221).
1885.	Van't Hoff, Jacobus Henricus (Holland), published his studies on chemical equilibria, including his law giving the effect of changes in temperature (§ 219).
1886.	Moissan, Henri (France), isolated fluorine by electrolysis of a solution of potassium hydrogen fluoride in liquid hydrogen fluoride (§ 197).
1887.	Arrhenius, Svante (Sweden), published his ionic theory (§ 250).
1894.	Van't Hoff (Holland) and Le Bel (France) independently found the relationship of the optical activity of organic compounds to the arrangement of the atoms in their molecules. This work gave rise to the modern "space models" of organic molecules.
1894.	Ramsay, Rayleigh, and Travers (England) discovered the inert gases.
1895.	Roentgen, William Conrad (Germany), discovered X-rays. This purely physical discovery exerted a great influence in the subsequent development of chemistry.
1897.	Thomson, Sir Joseph John (England), published his early researches on the properties of electrons. This marked the beginning of modern work on the constitution of atoms.
1898.	Curie, Marie Slowdowska (France), discovered radium, the first radioactive element. This was the beginning of subsequent remarkable developments in the field of radioactivity (§ 601).
1902, 1903.	Rutherford, Sir Ernest (England), identified the three kinds of rays emitted by radioactive elements, and studied their characteristics (§ 601); discovered the law that determines the rate of radioactive disintegration (§ 601).

1911.	Millikan, Robert (America), first isolated an electron, and studied its motion in an electric field. Calculations based on this work give us our most accurate figure for the *Avogadro's number*—the number of molecules in a gram-molecule (6.06×10^{23}).
1913.	Bragg and Bragg (England) published their early reasearches on a method for determining the arrangement of atoms in crystals, with the aid of X-rays.
1913.	Soddy, Frederick (England), and others discovered the law which states the effect of the loss of an alpha- or beta-particle on the position of an element in the periodic table (§ 601). As a result of this generalization, we are now able to *group the radioactive elements into three distinct lines of descent* (§ 601).
1913.	Moseley, H. G. T. (England), determined the atomic numbers of many elements, and thus confirmed their positions in the periodic table, through obesrvations of their X-ray spectra (§ 171).
1917.	Hull, Albert W. (America), published his method for determining the arrangement of atoms in crystals, by means of X-rays (§ 30). His method is an improvement over that of Bragg and Bragg in that it does not require large crystals, but makes use of crystalline powders.
1919.	Langmuir, Irving (America), published his theory (§ 188) of the structure of atoms. This is a development of the ideas of G. N. Lewis, and, though incomplete, probably includes some ideas that will help construct the theory of the future.
1919, 1920.	Aston, F. W. (England), developed the positive-ray analysis of J. J. Thomson, as a means for determining the relative masses of isotopes. For the first time, it became clear that the atoms of a given element are not all alike, but may differ in mass, and in the characteristics depending on mass, while remaining identical in chemical properties (§ 172).
1920.	Siegbahn (Sweden) increased the accuracy of measurement of X-ray spectra about 100-fold. Thus it became possible to measure the "energy levels" represented by the different lines in each spectrum—an important advance in elucidating the structure of atoms.
1921.	Rutherford (England) obtained the spectrum of hydrogen, by subjecting the atoms of nitrogen and aluminum to bombardment by alpha-particles emitted by radium. This is perhaps the first instance of the artificial transmutation of one element into another (§ 601).
1923.	Lewis, Gilbert Newton (America), published a summary of more than twenty years of research, largely performed

> at the University of California, on the "Free Energy of Chemical Substances." The development of this subject is one of the most important problems before the chemists of to-day. As data accumulate, we shall be able to calculate the degree of attainable completeness of important reactions under widely differing experimental conditions, in advance of actual trial.

Chemistry is an international science. Its foundations were laid in England, France, and Scandinavia. In its subsequent development, Germany played a prominent part; while chemists of Italy, the United States, and other countries made important contributions. At present, America affords the best material equipment for chemical investigations. The American Chemical Society, with about 15,000 members, is the largest organization of its kind in existence. In actual number of chemical investigations published, America now leads the world; and among these are a reasonable proportion of the most noteworthy advances of recent years.

F. ELECTRICAL UNITS

For a comparison of the simpler metric and English units, see page 15. The calorie is defined in Appendix II.

An understanding of the common electrical units is best obtained by noting that their definitions follow a definite logical sequence, beginning with the unit of force.

The unit of **force** (the **dyne**) is that force which, acting continuously for one second on a mass of one gram, can produce in the latter a change in velocity of one centimeter per second

↙

The unit of **work** or **energy** (the **erg**) is the work that is done, or the energy that is expended, when a body moves through a distance of one centimeter, under the influence of a force of one dyne. Energy equivalent to 10,000,000 ergs is called a **joule**.

↓

The unit **rate of work** (namely, unit **power**) is the **watt**. It is work done at the rate of one joule per second.

The unit of **electrical quantity** is the **coulomb**. It is the quantity of electricity that must be passed through a solution of silver nitrate (with proper precautions) to deposit 0.001118 g. of silver on the cathode. This corresponds to the passage of 6.06×10^{23} electrons.

↓

The unit of **electrical current** is the **ampere**. It corresponds to the passage of one coulomb of electricity each second.

↘ ↙

Electrical potential or **electromotive force** (sometimes improperly called voltage) is measured by the energy that must be expended in order to transfer electricity through a circuit. The unit of electrical potential is the **volt**. It is the potential existing between two points when one joule of energy needs to be expended for each coulomb of electricity transferred through the intervening portion of the circuit (or when energy needs to be expended at the rate of one watt for each ampere of current maintained in the circuit). The electromotive force of a standard Weston cell (§ 426), is 1.0183 international volts, at 20° C.

Volts = Joules/Coulombs = Watts/Amperes.

The **electrical resistance** of a circuit is measured by the electromotive force that must be applied in order to maintain a given current through the circuit. The unit of resistance is the **ohm.** It [illegible] the resistance of a circuit in which an electromotive force of one volt will maintain a current of one ampere.

Ohms = Volts/Amperes

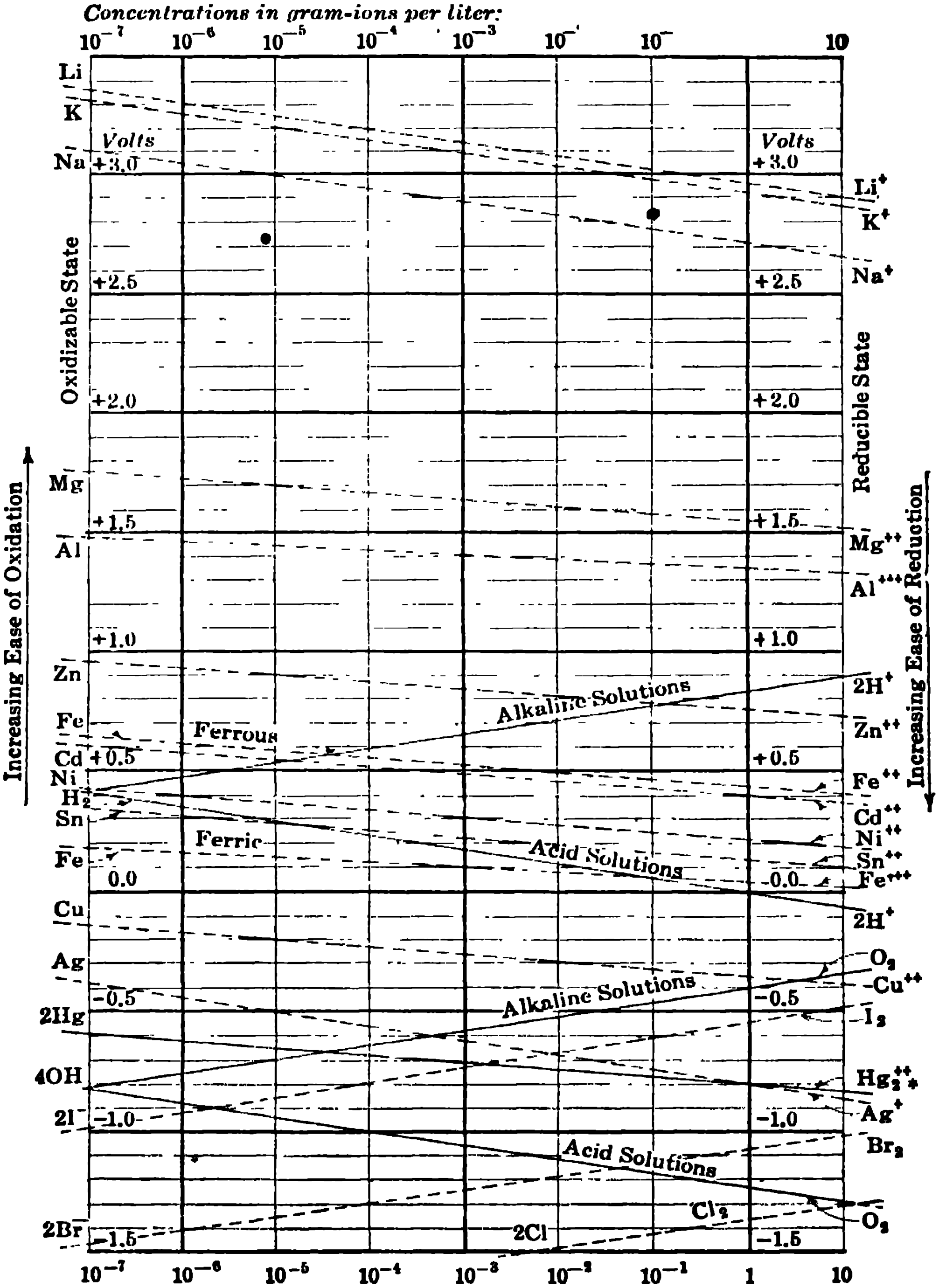
The reciprocal of resistance is called **conductance** or **conductivity.** Its unit is the **mho.** Thus a circuit with a resistance of 100 ohms has a conductance of 0.01 mhos.

G. EQUILIBRIUM POTENTIALS

See §§ 422-424. This chart has many uses but briefly touched upon in the text: To determine the potential that will be set up when given elements are used in constructing a primary cell; to show the minimum electromotive force necessary to separate a given metal by electrolysis from a solution of given concentration; to indicate which of several possible reactions will predominate at each electrode during electrolysis; to indicate the order of replacement of one metal by another, and the degree of completeness of such replacement; to show the concentrations under which two different ions may remain in equilibrium with each other. The data here charted, with the exception of those for Mg, Al, and Hg, are from Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances."

The zero of potential is here taken as that of a hydrogen electrode (§ 273) dipping into a solution normal with respect to hydrogen-ion.

EQUILIBRIUM POTENTIALS



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* Mercurous mercury exists in solution as a double bivalent ion, $(Hg_2)^{++}$. Accordingly, such a salt as mercurous chloride ought always, in strict accuracy, to be written Hg_2Cl_2 and not HgCl.

H. HEAT VALUES OF FUELS

The unit of heat is the **calorie**. This is the quantity of heat needed to raise the temperature of one gram of water one degree centigrade (more accurately from 15° C. to 16° C.). In some instances, the large Calorie (distinguished by being capitalized) is used. This is 1000 calories. In the English system, the unit of heat is the **British thermal unit** (B.T.U.). This is the quantity of heat needed to raise the temperature of one pound of water 1° F. It is 252 calories.

Gaseous Fuels

	Small Calories per Gram	*B.T.U. per Pound*
Acetylene	11,923	
Carbon monoxide	2,435	
Coal gas	about 11,000	
Ethylene	12,143	
Hydrogen (to liquid H_2O)	33,900	
Methane	13,063	
Producer gas	about 600	
Water gas	4,500	

Liquid Fuels

Benzene	9,977	
Ethyl alcohol	7.050	
Fuel oil, heavy petroleum residue	10,350	
Gasoline	about 11,250	
Kerosene	about 11,100	
Methyl alcohol	5,307	
Paraffin oil	9,800	
Petroleum	10,800–11,100	

Solid Fuels

Coal, lignite, low grade	3,247	5,845
Coal, lignite, high grade	6,764	12,175
Coal, bituminous, low grade	6,088	10,958
Coal, bituminous, high grade	7,852	14,134
Coal, semi-anthracite	7,612	13,702
Coal, anthracite	7,000	12,700
Paraffin	10,340	18,300
Peat, air dried	5,000	8,900
Wood, pine	5,000	8,900

I. OTHER NAMES FOR CHEMICAL SUBSTANCES

(Names not listed here should be sought in the index)

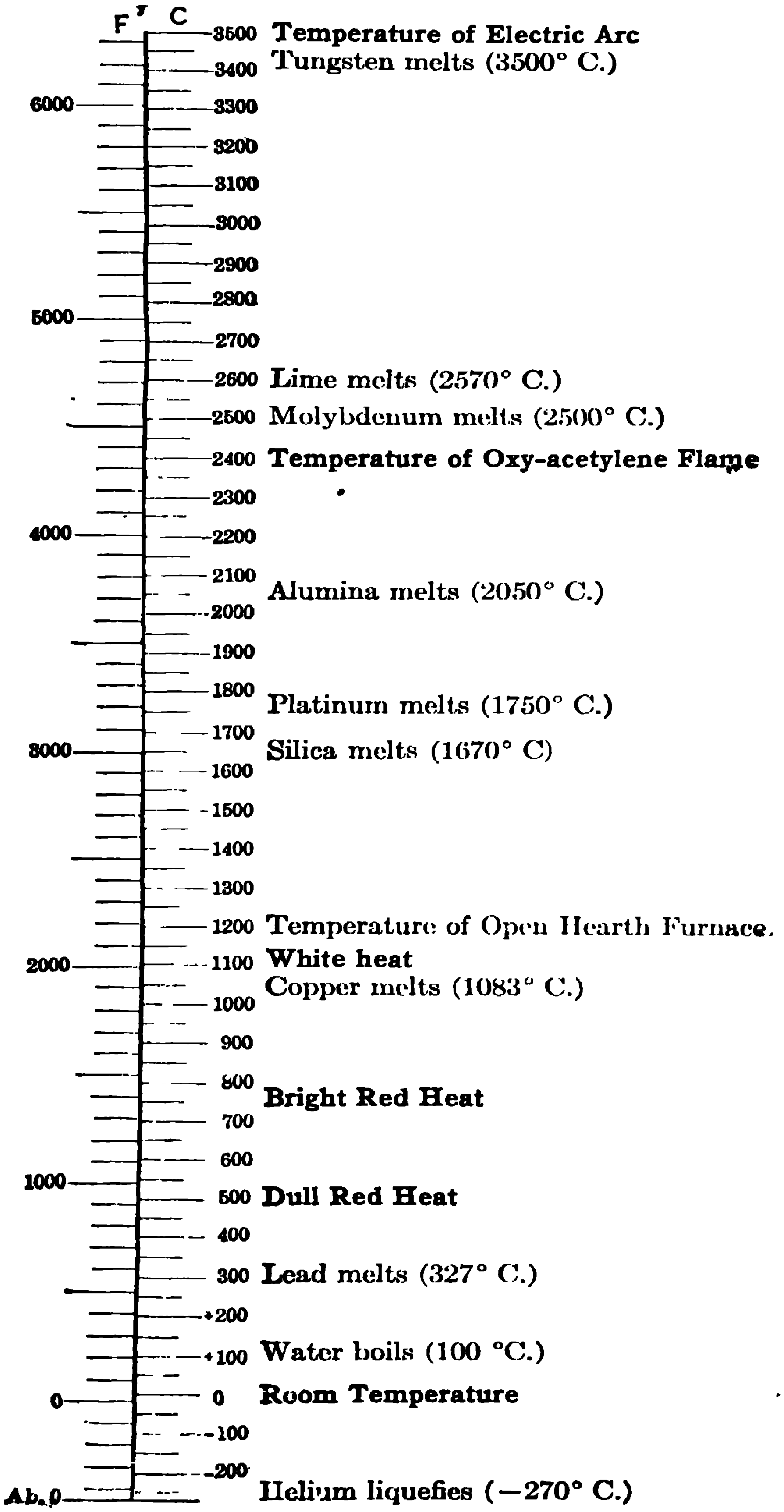
Alabaster.	A form of gypsum, $CaSO_4.2H_2O$.
Alum.	Potassium aluminum sulfate, $KAl(SO_4)_2.12H_2O$.
Alum, burnt.	Alum, dehydrated, with some loss of SO_3, by heating.
Alum, chrome.	Potassium chromium sulfate, $KCr(SO_4)_2.12H_2O$.
Alum, ferric.	Potassium ferric alum, $KFe(SO_4)_2.12H_2O$.
Alunite.	A basic aluminum sulfate mineral.
Ammonia water.	Ammonium hydroxide solution.
Ammonium polysulfide solution.	Yellow ammonium sulfide, a solution of sulfur in ammonium sulfide.
Antichlor.	Sodium thiosulfate.
Apatite.	A mineral consisting of calcium phosphate, in combination with a small proportion of calcium chloride, or calcium fluoride.
Aqua ammonia.	A solution of ammonium hydroxide.
Aqua fortis.	Nitric acid, HNO_3.
Aqua regia.	A mixture of hydrochloric acid and nitric acid.
Aragonite.	A form of calcium carbonate, $CaCO_3$.
Argols.	Impure potassium acid tartrate, $KHC_4H_4O_6$, obtained from the dregs of wine casks.
Arsenic, white.	Arsenious oxide, As_2O_3.
Baking soda.	Sodium bicarbonate, $NaHCO_3$.
Barite.	Native barium sulfate, $BaSO_4$.
Baryta water.	A solution of barium hydroxide.
Bismuth subnitrate.	A basic bismuth nitrate of variable composition.
Blanc fixe.	Barium sulfate, $BaSO_4$.
Bleaching powder.	Calcium chloride-hypochlorite, $CaCl(OCl)$.
Bluestone.	Crystalline copper sulfate, $CuSO_4.5H_2O$.
Blue vitriol.	*See* bluestone.
Boracic acid.	Boric acid, H_3BO_3.
Borax glass.	Borax, dehydrated and fused by heating.
Brimstone.	Sulfur.
British gum.	Dextrin.
Bromine water.	A solution of bromine in water.
Burnt lime.	Calcium oxide, CaO.
Butter	(of antimony or zinc). Refers to the chloride of the metal.
Calcite.	Native crystalline, calcium carbonate, $CaCO_3$.
Calomel.	Mercurous chloride, Hg_2Cl_2.
Carbolic acid.	Phenol, C_6H_5OH.
Carmine.	*The coloring matter of cochineal, adsorbed ("laked") on aluminum hydroxide.*
Caustic	(lime, soda, potash). The hydroxide of the given alkali or alkaline earth metal.
Celestite	A mineral, strontium sulfate, $SrSO_4$.
Chalk.	A mineral, impure calcium carbonate, $CaCO_3$. Blackboard crayons are now largely made of calcium sulfate.

Chloride of lime.	*See* bleaching powder.
Choke damp.	Carbon dioxide.
Chrome yellow.	Lead chromate.
Cinnabar.	A mineral, mercuric sulfide.
Copperas.	Ferrous sulfate, $FeSO_4.7H_2O$.
Corrosive sublimate	Mercuric chloride, $HgCl_2$.
Cream of tartar.	Potassium acid tartrate, $KHC_4H_4O_6$.
Dakin's solution.	A solution of sodium hypochlorite and chloride, usually containing boric acid.
Epsom salts.	Magnesium sulfate, $MgSO_4$.
Fire damp.	Methane, CH_4.
Flowers	(of sulfur, tin, zinc). Finely divided sulfur, produced by distillation; or the oxide of the metal named.
Fluorite.	A mineral, calcium fluoride.
Fuming nitric acid.	Nitric acid of a concentration greater than that of the usual "concentrated" (65%) acid. In consequence of partial decomposition, it is colored yellow, from dissolved NO_2.
Fuming sulfuric acid.	A solution of sulfur trioxide in concentrated sulfuric acid.
Fusel oil.	A mixture of poisonous higher alcohols, obtained in the purification of ethyl alcohol by fractional distillation.
Glauber's salt.	Sodium sulfate, $Na_2SO_4.10H_2O$.
Halite.	Native sodium chloride, $NaCl$.
Iceland spar.	A transparent, crystalline variety of native calcium carbonate, $CaCO_3$.
Iridosmine.	A natural alloy of iridium and osmium, remarkable for its hardness and resistance to acids.
Juane brilliant.	Cadmium sulfide, CdS.
Labarraque's solution	A solution of sodium hypochlorite, first used as an embalming fluid.
Laughing gas.	Nitrous oxide, N_2O.
Limewater.	A solution of calcium hydroxide, $Ca(OH)_2$.
Lunar caustic.	Silver nitrate, $AgNO_3$.
Magnesia alba (Magnesia usta).	A light, fluffy form of magnesium oxide, MgO.
Marsh gas.	Methane, CH_4.
Marble.	A native form of calcium carbonate.
Meerschaum.	A hydrated magnesium silicate, related in chemical composition to talc and asbestos.
Microcosmic salt.	Sodium, hydrogen, ammonium phosphate, $NaNH_4HPO_4$.
Mohr's salt.	Ferrous ammonium sulfate, $FeSO_4.(NH_4)_2SO_4.6H_2O$.
Monazite.	A complex mineral serving as a source of cerium and other rare earth elements.
Muriatic acid.	*Hydrochloric acid.*
Muriate	(of ammonium, potassium, etc.). The chloride of the metal named.
Nordhausen acid.	*See* fuming sulfuric acid.
Niter.	Potassium nitrate. In ancient times the word was also applied to potassium carbonate.
Ocher.	Ferric oxide, Fe_2O_3.

Oil of vitriol.	Concentrated sulfuric acid.
Oleum.	*See* fuming sulfuric acid.
Orpiment.	A mineral, arsenic trisulfide, As_2S_3.
Pearl ash.	Potassium carbonate, K_2CO_3.
Permanent white.	Barium sulfate, $BaSO_4$.
Petroleum ether.	A mixture of the lower-boiling paraffin hydrocarbons (§ 344).
Phlogiston.	A hypothetical substance, which before the time of Lavoisier was thought to be concerned in oxidation and reduction. A substance which was burned or oxidized was assumed to lose phlogiston in the process.
Pitchblende.	A complex uranium mineral, which served as the first source of radium.
Plumbago.	Graphite, C.
Prussic acid.	Hydrocyanic acid, HCN.
Purple of Cassius.	A form of colloidal gold, adsorbed on stannic oxide, or some other finely divided, white material.
Pyrene.	A trade name for carbon tetrachloride, CCl_4, used in fire extinguishers.
Pyrogallic acid.	Pyrogallol, $C_6H_3(OH)_3$, used in alkaline solution, as an absorbent for oxygen (§ 280).
Pyroligneous acid.	Impure acetic acid, produced by destructive distillation of wood.
Pyrosulfates.	Salts of the hypothetical pyrosulfuric acid, $H_2S_2O_7$.
Pyrophosphates.	Salts of the hypothetical pyrophosphoric acid, $H_4P_2O_7$.
Pyrolusite.	Manganese dioxide, MnO_2.
Quicklime.	Calcium oxide, CaO.
Realgar.	A mineral, arsenic disulfide, As_2S_2.
Red prussiate of potash.	Potassium ferricyanide, $K_3Fe(CN)_6$. Intensely poisonous.
Regulus.	Antimony, or some other metal, prepared from its ores by reduction.
Rochelle salt.	Potassium sodium tartrate, $KNaC_4H_4O_6$.
Rock salt.	An *impure form of sodium chloride, identical with the mineral halite.*
Saccharin.	An organic compound, benzolsulfimide, $C_6H_4.CO.NH.SO_2$, several hundred times as sweet as sugar.
Sal ammoniac.	*Ammonium chloride,* NH_4Cl.
Sal soda.	*Sodium carbonate,* $Na_2CO_3.10H_2O$.
Sal tartar.	Potassium carbonate, K_2CO_3.
Sal volatile.	Ammonium carbonate, $(NH_4)_2CO_3$.
Saleratus.	Sodium or potassium bicarbonate, $NaHCO_3$ or $KHCO_3$.
Salt, common.	Sodium chloride, NaCl.
Salt of lemon.	Potassium acid oxalate, KHC_2O_4.
Salt of tartar.	Potassium carbonate, K_2CO_3.
Saltpeter.	Potassium nitrate, KNO_3.
Saltpeter, Chile.	Sodium nitrate, $NaNO_3$.
Scheele's green.	Cupric hydrogen arsenite, $CuHAsO_3$.
Soluble glass	(water glass). Sodium silicate, (§ 410).

Silvite.	Native potassium chloride, KCl.
Slaked lime.	Calcium hydroxide, $Ca(OH)_2$.
Spirits.	Ethyl aclohol.
Spirits of ammonia.	A solution of ammonia gas in alcohol.
Spirits of ammonia, aromatic.	A solution of ammonia gas and ammonium carbonate in alcohol.
Spirits, Cologne.	Ethyl alcohol.
Spirits of hartshorn.	A solution of ammonia and ammonium carbonate in alcohol.
Spirits, methylated.	Ethyl alcohol, denatured with methyl alcohol.
Spirits, sweet, of niter.	A solution of ethyl nitrite, $C_2H_5NO_2$, in alcohol.
Spirits, wood.	Methyl alcohol, CH_3OH.
Starch gum.	Dextrin.
Stibnite.	A mineral, antimony trisulfide, Sb_2S_3.
Sulfhydrate	(of ammonium, potassium, etc.). The acid sulfide of the given metal; as NH_4HS.
Tartar.	Potassium tartrate, $K_2C_4H_4O_6$.
Tartar emetic.	Potassium antimonyl tartrate, $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$.
Technical.	(As produced on a commercial scale, and usually impure.)
Tin salt.	Crystallized stannous chloride, $SnCl_2.2H_2O$; or a double salt, stannous ammonium chloride.
Tinstone.	A mineral, cassiterite, SnO_2.
Topaz.	A complex aluminum silicofluoride.
Turnbull's blue.	A blue pigment, approximating the composition of ferrous ferricyanide, $Fe_5C_{12}N_{12}$, use for "blueing" in laundering.
Turpeth.	Mercurous sulfate, Hg_2SO_4.
Ultramarine.	A violet, blue, or blue-green pigment, identical with blue mineral *lapis lazuli*, and made by heating clay with sodium sulfate, charcoal, and sulfur. The material is of variable composition, and its color presumably a colloidal phenomenon.
Ultramarine yellow.	Barium chromate, $BaCrO_4$.
Venetian red.	Ferric oxide, Fe_2O_3.
Verdigris.	A basic cupric acetate. "Crystallized verdigris" is the normal acetate.
Vitriol.	Refers to a metallic sulfate. Blue vitriol is cupric sulfate, $CuSO_4.5H_2O$; green vitriol is ferrous sulfate, $FeSO_4.7H_2O$; *white vitriol is zinc sulfate*, $ZnSO_4.7H_2O$.
Vitriol, oil of.	Concentrated sulfuric acid.
Whiting.	Chalk, calcium carbonate, $CaCO_3$.
Yellow prussiate of potash.	Potassium ferrocyanide, $K_4Fe(CN)_6.H_2O$. In contrast with the red prussiate of potash, $K_3Fe(CN)_6$, it is practically non-poisonous.

J. TEMPERATURE SCALES (see page 23)



K. BIBLIOGRAPHY

Interesting articles on chemical topics are constantly appearing in the popular magazines. Refer to appropriate headings in " Poole's Index " and Wilson's "Readers' Guide." Especially, consult recent issues of "Smithsonian Reports."

Beginners are often helped by supplementary reading in a high-school text-book. Excellent presentations are those by Brownlee and others; Conant and Black; Gray and others; McPherson and Henderson; and Morgan and Lyman. The reference library should also include recent college texts: Hildebrand; Holmes; McPherson and Henderson; Norris; and Alexander Smith.

The following bibliography lists books suitable for popular reading, on topics included in the present text; and, in addition, a few standard reference books. An edition of 1920 or later is available, unless otherwise indicated.

Popular Books on General Science

Berthoud.	Pioneers of Progress (Macmillan).
Hammond.	Stories of Scientific Discovery (Cambridge Univ. Press).
Harrow.	Contemporary Science (Boni & Liveright, New York).
Kendall.	Civilization and the Microbe (Houghton Mifflin).
Lawson.	The New Physics (Dutton & Co.).
Slosson.	Chats on Science (Century Co.).
	Keeping Up with Science (Harcourt, Brace & Co.)
Whetham.	Recent Development of Physical Science (Blakiston's).
Whetham and Whetham.	Cambridge Readings in the Literature of Science (Cambridge Univ. Press).
Whitney.	Soil and Civilization (Van Nostrand).
Woodruff.	Development of the Sciences (Yale Univ. Press).

Popular Books on Chemistry

Armstrong.	Chemistry in the Twentieth Century (Macmillan).
d'Albe.	Contemporary Chemistry (Van Nostrand).
Duncan.	Chemistry of Commerce (1908) (Harper & Bros.).
Duncan.	Chemical Problems of To-day (1911) (Harper & Bros.).
Engineering Foundation.	Research Narratives (Williams & Wilkins Co., Baltimore).
Findley	Chemistry in the Service of Man (Longmans, Green).
Harrow.	Famous Chemists of Our Time.
Hendrick.	Everyman's Chemistry (Harper & Bros.).
Howe.	Chemistry in Industry (Chemical Foundation).
Martin.	Modern Chemistry and Its Wonders (Van Nostrand).
Pilcher and Butler-Jones.	What Industry Owes to Chemical Science (Van Nostrand).
Slosson.	Creative Chemistry (The Century Co.).
Stillman.	The Story of Early Chemistry (D. Appleton & Co.).

Tilden.	Chemical Invention and Discovery in the Twentieth Century (E. P. Dutton & Co.). Famous Chemists (E. P. Dutton & Co.).

Treatises on Inorganic Chemistry

Friend.	Textbook on Inorganic Chemistry * (Longmans, Green).
Mellor.	Comprehensive Treatise on Inorganic Chemistry and Theoretical Chemistry * (Longmans, Green).
Roscoe and Schorlemmen.	Treatise on Chemistry (Vols. I and II) (Macmillan).

Organic Chemistry

Chamberlain.	Organic Chemistry (Blakiston's).
Holleman-Walker.	Organic Chemistry (Wiley & Sons).
Lowy and Harrow.	Organic Chemistry (Wiley & Sons).

An interesting simplified presentation is:

Remsen.	Organic Chemistry (Holt & Co.).

* In a series of volumes not yet complete.

Analytical Chemistry

Treadwell-Hall.	Analytical Chemistry (Wiley & Sons).

Physical Chemistry

Getman.	Outlines of Theoretical Chemistry (Wiley & Sons).
Morgan.	Elements of Physical Chemistry (1918) (Wiley & Sons).

For a presentation emphasizing developments of the past few years:

Millard.	Physical Chemistry (McGraw-Hill).

More advanced in character:

Washburn.	Physical Chemistry (McGraw-Hill).

Applications of Chemistry in Industry

Liddell.	Handbook of Chemical Engineering (2 vols.) (McGraw-Hill).
Molinari.	General and Industrial Chemistry (1913) (Van Nostrand).
Rogers.	Industrial Chemistry (Van Nostrand).

Handbooks of Numerical Data

Comey-Hahn.	Dictionary of Chemical Solubilities (Macmillan).
Hodgeman and Lange.	Handbook of Chemistry and Physics (Chemical Rubber Co.).
Kaye and Laby.	Tables of Physical and Chemical Constants (1918) (Longmans, Green).
Olsen.	Chemical Annual (1913) (Van Nostrand).

Seidell.	Solubility of Inorganic and Organic Substances (1907) (Van Nostrand).

Catalyzers and Catalysis

Effront-Prescott.	Biochemical Catalysts in Life and Industry (Wiley & Sons).
Falk.	Catalytic Action (Chemical Catalogue Co.).
Henderson.	Catalysis in Organic Chemistry (Longmans, Green).
Rideal-Taylor.	Catalysis in Theory and Practice (Macmillan).
Sabatier-Reid.	Catalysis in Organic Chemistry (Van Nostrand).

Food and Nutrition

Harrow.	Vitamins. What to Eat.
Hawk.	What We Eat and What Happens to It (Popular) (1919) (Harper & Bros.).
Sherman.	Chemistry of Food and Nutrition (Macmillan). The Vitamins (Macmillan). Food Products (Macmillan).

Colloids

Alexander.	Colloid Chemistry (Van Nostrand).
Arndt-Katz.	Colloids in the Industrial Arts (Popular) (Chemical Publishing Co.).
Bancroft.	Applied Colloid Chemistry (McGraw-Hill).
Bechhold-Bullowa.	Colloids in Biology and Medicine (Van Nostrand).
Bogue.	Theory and Application of Colloidal Behavior (2 vols.) (McGraw-Hill).
Burton.	Physical Properties of Colloidal Solutions (Longmans, Green).
Ostwald-Fischer.	Handbook of Colloid Chemistry (1915) (Blakiston's). Theoretical and Applied Colloid Chemistry (1917) (Wiley & Sons).
Zsigmondy.	Colloids and the Ultramicroscope (1909) (Wiley & Sons).
Zsigmondy and Spear.	The Chemistry of Colloids (1917) (Wiley & Sons).

Modern Theory of the Structure of Atoms

Berthoud.	New Theories of Matter and the Atom (Macmillan).
Comstock and Troland.	The Nature of Matter and Electricity (Van Nostrand).
Lukiesch.	Foundations of the Universe (Van Nostrand).
Mills.	Within the Atom (Van Nostrand).
Russell, Bertrand.	A B C of Atoms (Dutton & Co.).

The Electron Theory

d'Albe.	The Electron Theory (Popular) (1906) (Longmans, Green).
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ANSWERS TO PROBLEMS IN BODY OF TEXT (PART I)

Figures in bold-faced type refer to numbered sections.

27. 0.2 cc.; 4 times as dense. **35.** 1+2.09=1.91+1.18; 2 g.; wt. *A*+wt. *B*=wt. *C*+wt. *D*. **38.** 83. **42.** 118; 10 moles; 10 times as heavy; 5 times as heavy. **51.** 4 moles sodium peroxide; 1 mole=32 g. oxygen. **70.** 4 moles=72 g. water; 28 g. silicon; 130 g. zinc. **72.** 3 cases of action liberating hydrogen, and 3 cases of other gases being liberated. **74.** no change; contracts one-half; contracts one-third; contracts one-seventh; 15 molecules hydrogen, 10 molecules ammonia; $2\frac{1}{2}$ moles oxygen. **88.** 5 moles=90 g. water. 1 mole=153 g. $CuSO_4$; 36% water. **103.** (1) 36.45 g. HCl; 60 g. $HC_2H_3O_2$; 49 g. H_2SO_4; 32.67 g. H_3PO_4. (2) 6 g. **105.** (11) Acetic acid and hydrochloric acid. **108.** (15) 2 moles=36 g. water, for 1 mole= 58 g. magnesium hydroxide; or 0.62 g. for 1 g. **111.** (28) 0.0329. (29) 0.23 g. **112.** (31) 56 g.; 0.89 g. (34) 2 moles. (35) $NaHSO_4$. (36) 2 moles. **115.** (46) 142 g. (47) 8 g. **139.** (2) 17 g.; 22.4 l.; 0.76 g. (4) 3.17 g. **140.** (5) 0.005. (6) 0.01. (7) 55.5. (8) 1.95. (10) 2200 cc. (11) 44.6 moles. (12) 0.005. (13) 1000; 44.6 moles. **141.** (14) 16.6 g. **142.** (15) 10, 30, 5 cu. ft. (16) 5 cc. NH_3. (17) increase, 20 cc. **145.** (19) 29.16 mg. (20) 729 g. (21) 0.342; 8.23%. **146.** (22) 20%. (23) 1200 g.; 328 g. (24) 24.4%. (25) 1.46; 1.40. (26) 4.84 g. (28) 2.42 moles. (29) 2.42 moles; 88.1 g. HCl; 188 cc. (30) 12.6 g. (31) 670 cc. (32) 43.9 g. (33) 38.4 cc. **147.** (34) 36 mg. **149.** (35) 0.2 N; 0.1 M. (36) 0.4 N. (37) 7.1 g. **150.** (38) 7.5 cc. (39) 500 cc. (40) KI; 0.5 mg.-eq.; 0.0005 mole. **153.** (1) 5.52 g./l. (2) 26. (3) 17.032; 0.76 g./l. **155.** (4) Cl_2. **156.** (7) 44.6. **157.** (8) −0.37°. **158.** (9) Approx. at. wt.=85. **159.** (11) 2900 cals. (12) Iron. **160.** (13) NH_4Cl; $N_2H_8Cl_2$· $N_3H_{12}Cl_3$. **162.** (15) 55.83.

SOLUBILITY OF BASES AND SALTS IN WATER AT 18° C

	Li	Na	K	Mg	Ca	Sr	Ba	Fe'	Fe''	Cu'	Zn	Pb	Ag	Hg'	Hg''
F	0.27* 0.1042	4.4 1.048	92.3 15.89—2aq	0.0076** 0.0014	0.0016 $0.0_{3}205$	0.012* $0.0_{3}93$	0.163* 0.0093	*			1.6 0.155—4aq	0.0641* 0.0026	185 14.32	Decomp	Decomp.
Cl	77.0 18.16	35.9 6.14	33.4 4.48	54.1 5.68—6aq	72.5 6.51—6aq	52.8 3.33—6aq	35.2 1.69—2aq	41.5 3.27—4aq	89.8 2.76—12aq	75.6 5.62—2aq	362 26.54—1½aq	0.914* 0.0329	$0.0_{3}15$** $0.0_{4}11$	$0.0_{3}2$** $0.0_{5}43$	7.39 0.273
Br	174.0 20.02	89.0 8.65—2aq	64.1 5.38	96.1 5.21—6aq	141 7.05—6aq	98 3.96—6aq	103 3.46—2aq	53.5 2.48—6aq	s —6aq	v.s. —4aq	441 19.59—2aq	0.804* 0.0219	$0.0_{4}85$** $0.0_{5}45$	$0.0_{5}4$** $0.0_{7}7$	0.4 0.0111
I	163.0 12.17	176.7 11.79—2aq	142.6 8.59	148 5.32—8aq	203 6.9[illegible]—6aq	176.8 5.16—6aq	195	s			432 13.55	0.066 0.0014	$0.0_{6}3$** $0.0_{7}13$	$0.0_{7}2$ $0.0_{9}31$	**
ClO₃	313.5 34.6	97.0 9.11	6.7 0.546	[illegible] 6.8[illegible]—6aq	177.8 8.59—2aq	175.0 6.88	35.5 1.1[illegible]—1aq	s	s	164 7.12—4aq	198.8 8.55—4aq	151.3 4.05—1aq	10 0.52	**	Decomp
BrO₃	153.7 11.4	34.0 2.25	6.5 0.389		85 2.87—1aq	33 0.95—1aq	0.61 0.0155—1aq	s	57.5	s	58 1.8—6aq	1.34 0.029	0.144* 0.0061	Decomp	16
IO₃	80.3 4.41	8.5 0.429	7.5 0.350	8.22 0.22—4aq	0.26* $0.0_{2}67$—6aq	0.026* $0.0_{3}60$	0.021* $0.0_{3}43$—1aq	*	*	0.121* 0.0033	0.9* 0.022	0.0019** $0.0_{4}34$	0.004** $0.0_{4}14$	**	**
NO₃	70.3 10.18—3aq	86.0 10.11	29.6 2.93	7[illegible].2 4.94—6aq	121.2 7.39—4aq	67.6 3.20—4aq	8.8 0.336	46.5(24°) 2.58—9aq	s	120 6.40—6aq	115.1 6.08—6aq	50.7 1.532	204 12.0	Decomp	v.s.
SO₄	34.3 3.12—1aq	16.8 1.182—10aq	10.73 0.616	34.6 2.88—7aq	0.202* 0.015—2aq	0.0114** 0.0[illegible]2	$0.0_{3}23$** $0.0_{4}99$	26.4 1.74—7aq	*	19.0 1.25—5aq	53.0 3.28—7aq	0.0041** $0.0_{3}14$	0.775 0.0248	0.06 0.0012	Decomp
CrO₄	111.0 8.54—2aq	77.5 4.78—6aq	62.8 3.23	72.3 5.15—7aq	2.34 0.150	0.12* 0.0059	$0.0_{3}38$** $0.0_{4}15$	0.022* 0.0012—2aq		**	**	$0.0_{4}2$** $0.0_{6}2$	0.0025** $0.0_{4}75$	*	Decomp
C₂O₄	6.24(25°) 0.612	3.5 0.261	37.7(25°) 2.27—1aq	0.03* $0.0_{2}27$—2aq	$0.0_{3}56$** $0.0_{4}44$	$0.0_{2}46$** $0.0_{3}26$	0.0086 $0.0_{3}38$—2aq		**	**	$0.0_{3}64$** $0.0_{4}42$—2aq	$0.0_{4}15$** $0.0_{5}51$	0.0035 $0.0_{4}12$	**	
CO₃	1.35 0.1823	19.5 1.840—10aq	111.5 8.08	0.095* 0.0113—3aq	$0.0_{2}1$** $0.0_{3}13$	0.0011** $0.0_{4}68$	0.0022** $0.0_{3}11$	**	Decomp	**	0.001** $0.0_{4}81$	$0.0_{3}11$** $0.0_{4}41$	0.003** $0.0_{3}11$	**	**
C₂H₃O₂	v.s. —2aq	47 5.73—3aq	245 25.0	v.s. —4aq	37.0 2.21—2aq	s	69.7 2.7[illegible]—[illegible]aq	s	basic 0.02(?)* 0.00[illegible]2	7.2 0.396—1aq	40(25°) 3.21—2aq	50(25°) 1.538—3aq	1.005 0.0602	0.75(13°) 0.029*	
OH	12.8 5.34—1aq	107.5 26.9—1aq	130 19.6—2aq	0.0084 0.0015	0.167 0.023	0.78 0.063—8aq	3.78 0.220—8aq	0.0067 $0.0_{3}8$	**	**	$0.0_{3}56$** $0.0_{4}56$	0.0155* $0.0_{3}64$	0.0022** 0.018	**	
PO₄	**	19.6 1.18—12aq	v.s.	*	**	**	*	**	**	** —3aq	** —4aq	**	0.0064** $0.0_{3}13$	**	**

See general statement of solubilities in § 426.

* The upper number gives the number of grams of solute (calculated as anhydrous) that will dissolve in 100 g. of water at 18° C. The lower number gives the number of moles of solute in 1000 g. of water. If the solid in equilibrium with the saturated solution is a definite hydrate (§§ 66, 126) the symbol aq., preceded by a figure, indicates the number of molecules of water of hydration.

The figures for the solubilities of slightly soluble substances have been abbreviated, thus, $0.0_{3}15$ means 0.00015. A star means a slightly soluble substance—solubility less than about 1 g. in 100 g. of water. A double star means an "insoluble" substance—solubility less than about 0.01 g. in 100 g. of water. s. means soluble; v.s. means very soluble.

THE PERIODIC TABLE

O		IA R_2O	IIA RO	IIIA R_2O_3	IVB RO_2	VB R_2O_5	VIB RO_3	VIIB R_2O_7				IB R_2O	IIB RO	IIIB R_2O_3	IVA RO_2	VA R_2O_5	VIA RO_3	VIIA R_2O_7
										1 H 1.008								
2 He 4.00		3 Li 6.94	4 Gl 9.1	5 B 10.9	Arrows indicate directions of increasing basic properties. Sloping lines indicate the degree of relationship between Extreme Groups (A) and Intermediate Groups (B): greatest for Group IV, decreasing in both directions, and nearly disappearing with Groups 1 and VII.										6 C 12.005	7 N 14.008	8 O 16.000	9 F 19.0
10 Ne 20.2		11 Na 23.00	12 Mg 24.32	13 Al 27.0											14 Si 28.1	15 P 31.04	16 S 32.06	17 Cl 35.46
INERT GASES		LIGHT METALS							Transition Group Valence Variable					HEAVY METALS		NON-METALS		
18 A 39.9		19 K 39.10	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96	34 Se 79.2	35 Br 79.92
36 Kr 82.92		37 Rb 85.45	38 Sr 87.63	39 Yt 89.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43 ? 99±	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92
54 Xe 130.2		55 Cs 132.81	56 Ba 137.37	57-72 Rare Earths 139-179		73 Ta 181.5	74 W 184.0	75 ? 188±	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.20	83 Bi 209	84 Po 210	85 ? 219±
86 Rn 222.4		87 ? 225±	88 Ra 226.0	89 Ac 230	90 Th 232.15	91 Pa 234.2	92 U 238.2											

The rare earth elements are:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	?	Sa	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ct

Valence Details: